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(54) Title: PHASE-TRANSFORMING AND SWITCHABLE METAMATERIALS

(57) Abstract: A new soft structure that uses a meso- or macro-scale elastic instability to generate a shape-memory effect similar to that of a ferroelastic material is described. The soft metastructure exhibits phase transition, switching of variants, and shape-memory. The class of materials presented are useful, since they are "shape-memory alloys" of arbitrarily low modulus and arbitrarily large remnant strain.

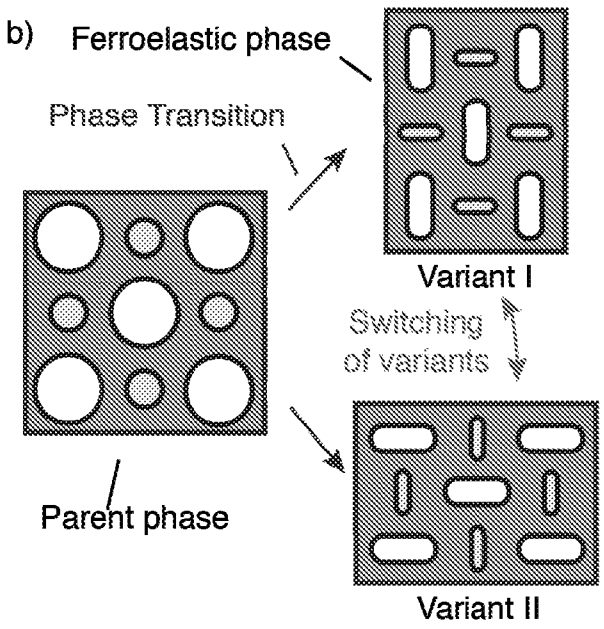

Figure 1B

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GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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PHASE-TRANSFORMING AND SWITCHABLE METAMATERIALS

RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Application No. 62/200,466, filed August 3, 2015, the entire content of which is expressly incorporated by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The present invention was made with United States government support under Grant No. DE-FG02-00ER45852 awarded by the Department of Energy and Grant No. DMR-1420570 awarded by the National Science Foundation. The United States government may have certain rights in this invention.

TECHNICAL FIELD

[0003] This technology relates generally to metamaterials. In particular, this invention relates to elastomeric materials with meso- or macro-scale features. The technology also relates phase changing and switchable metamaterials.

BACKGROUND

[0004] Many forms of matter—elements, molecules, and materials—can exist in multiple forms (phases), having different structures at the atomic and molecular scale, and different properties. The interconversions of these phases is a central concern in materials science and engineering, and can be classified as follows: transformations that exhibit discontinuity in the first derivative of the free energy with respect to some thermodynamic variable are characterized by large changes in thermodynamic properties (e.g. melting of a solid, smectic-A to nematic transition in liquid crystals, etc.), and are called first-order phase transitions. Transformations that exhibit continuity in the first derivatives of the free energy but

discontinuity in the second derivative are called second-order phase transitions. Examples include those in ferroelectrics, ferromagnetism, shape memory alloys, ferrorelastics, superconductivity, and superfluidity. A similar definition could be applied to higher-order phase transitions.

[0005] Although most examples of phase transitions involve structural rearrangements at the atomic/molecular scale, the underlying concept of a phase as a form of matter with defined structure can be applied at larger scales. Examples of phase transitions at the meso and macroscale include colloidal suspensions, 2D arrays of polymeric spheres, heat-shrinkable polymer patterns, mesoscale silicon rods embedded in a hydrogel, and slabs of elastomer with an array of holes. In broad terms, an emerging opportunity in materials science and engineering is to create phase-transforming materials by integrating materials—elastomers, liquids, metals, and even open spaces—through geometry and mechanics, at meso or macro scale.

[0006] Ferroelasticity is the mechanical analogue of ferroelectricity and ferromagnetism, and it is the underlying mechanism of shape-memory alloys. Ferroelastic materials are defined by its property of exhibiting a spontaneous strain under certain external stimulus. This spontaneous strain results in switchable variants of the material, which may be switched on application of an external field, such as stress. When cooled below a certain temperature—the "Curie temperature"—a ferroelastic material can develop spontaneous strains, and is said to be in a "ferroelastic phase". These microscopic spontaneous strain states—a.k.a. "variants"—are equivalent crystal structures in different orientations. An example of such variants is the different orientations of a tetragonal unit cell where the long axis points at different directions. A macroscopic external stress can induce "switching" between these variants throughout the material. As a result, the bulk material can be molded into different

macroscopic shapes depending on its history of loading, while maintaining a memory of its grain arrangements. When above the Curie temperature, however, the spontaneous strain disappears, and the material is said to be in a "paraelastic" or the "parent phase". Here, the different variants become one, and the material assumes a higher crystallographic symmetry. For example, the tetragonal unit cell discussed above becomes cubic. As a result, the material returns to its original shape, and thus generates a shape-memory effect.

[0007] Boyce and Bertoldi (*Phys. Rev. Lett.* 2007, 99, 084301) report a block of elastic material with an array of open through-holes having the same sizes that has been shown to realize a macroscopic "phase change" by applying pressure mechanically in the plane of the slab. *See,* **Figure 1A**. The block exhibits a change in stress-strain properties when the material is compressed beyond a certain threshold. The structure developed by Boyce and Bertoldi will phase transform, but since the two variants of their low-symmetry phase has no spontaneous strains, it's difficult to switch between them. Thus it cannot realize shape memory.

SUMMARY

[0008] A new soft structure that uses a meso- or macro-scale elastic instability to generate a shape-memory effect similar to that of a ferroelastic material is described.

[0009] In one aspect, a soft metamaterial includes a bulk elastic material having a substructure contained within the material, the substructure having a repeat unit of a size one or more orders of magnitude smaller than the bulk material, wherein the substructure is made of a material that is responsive to an external stimulus, and wherein a response of the substructure to an external stimulus induces in a mechanical deformation of the bulk elastic material.

[0010] In one embodiment, the external stimulus is selected from the group consisting of a change in ambient pressure, salt concentration/osmotic pressure, temperature, PH, applied external electric field, mechanical pressure, hydrostatic pressure and magnetic field.

[0011] In one or more embodiments, the repeat unit has a size in the range of about 1 μm to about 1 m, or a repeat unit has a size in the range of about 1 μm to about 1 cm, or a repeat unit has a size in the range of about 1 μm to about 1 mm. In one or more embodiments, the repeat unit has a size in the range of about 100 μm to 1 cm.

[0012] In one or more embodiments, the substructure includes a regular array of sealed holes or voids in an elastomeric body, wherein the array of holes or voids is isolated from the environment.

[0013] In one or more embodiments, the array of holes or voids includes an alternating arrangement of larger and smaller holes or voids.

[0014] In one or more embodiments, the internal pressure inside the array of holes or voids is at a sub-atmospheric pressure.

[0015] In one or more embodiments, the array of holes or voids are in an expanded state when the external pressure matches the sub-atmospheric pressure of the holes or voids and in a collapsed state when the external pressure is greater than the sub-atmospheric pressure of the of holes or voids.

[0016] In one or more embodiments, the substructure comprises a regular array of hydrogel pellets, wherein the hydrogel pellets are in communication with the environment and/or with one another.

[0017] In one or more embodiments, the hydrogel pellets are in a resting expanded state when the environment is at a first condition, e.g., salt concentration/osmotic pressure,

temperature, PH, applied external electric field, that forms a hydrated hydrogel pellet and in a collapsed state when the environment is at a second condition, e.g., salt concentration/osmotic pressure, temperature, PH, applied external electric field, that form a dehydrated or less hydrated hydrogel pellet.

[0018] In one or more embodiments, the array of hydrogel pellets comprises an alternating arrangement of larger and smaller hydrogel pellets.

[0019] In one or more embodiments, the substructure comprises an array of solid pellets with a high degree of thermal expansion.

[0020] In one or more embodiments, the array of solid pellets comprises an alternating arrangement of larger and smaller solid pellets.

[0021] In one or more embodiments, the solid pellets are in an expanded state at a first higher temperature and in a collapsed state at a second lower temperature.

[0022] In another aspect, a method of deforming a bulk material includes providing a soft metamaterial, comprising an elastic material having a substructure contained within the material, the substructure having repeat unit of size one or more orders of magnitude smaller than the bulk material, wherein the substructure is made of a material that is responsive to an external stimulus, and exposing the soft metamaterial to an external stimulus, wherein a response of the substructure to an external stimulus induces in a mechanical deformation of the bulk elastic material.

[0023] In one or more embodiments, the external stimulus is selected from the group of a change in ambient pressure, salt concentration/osmotic pressure, temperature, PH, applied external electric field or magnetic field.

[0024] In one or more embodiments, the substructure is selected from the group of sealed air pockets, hydrogel pellets and solid thermally expanding solid pellets.

[0025] In one or more embodiments, the substructure comprises an array of holes having an internal pressure, wherein the holes are in an expanded state when the external pressure matches the internal pressure of the of holes and in a collapsed state when the external pressure is greater than the internal pressure of the of holes; and changing the external pressure to induce a phase change from the expanded state to the collapsed state (or vice versa) in the material.

[0026] In another aspect, a method of inducing a phase change in a material includes providing a bulk elastic material having a substructure contained within the material, the substructure having repeat unit of a size one or more orders of magnitude smaller than the bulk material, wherein the substructure comprises an alternating arrangement of larger and smaller compressible elements, wherein the bulk elastic material is capable of taking on two different orientations when the bulk elastic material is under an internally generated compression; and applying a first external force to the bulk elastic material, wherein the material switches between orientations.

[0027] In yet another aspect, a method of inducing a phase change in a material includes providing a bulk elastic material having a substructure contained within the material, the substructure having repeat unit of a size one or more orders of magnitude smaller than the bulk material, wherein the substructure comprises an array of holes having an alternating arrangement of larger and smaller holes, the hole maintained at a pressure less than the ambient pressure, wherein the bulk elastic material is capable of taking on two different orientations when the bulk elastic material is under ambient pressure; and applying a first external force to the bulk elastic material, wherein the material switches between orientations.

[0028] In one or more embodiments, the bulk elastic material retains the new orientation after release of the first applied external force.

[0029] In one or more embodiments, the bulk elastic material reverts to the initial orientation upon application of a force perpendicular to the first applied external force.

[0030] In one or more embodiments, the compressible elements comprise hydrogel pellets with are in a tensile state due to dehydration, and the internal compressive forces arise from the transition of the hydrogel pellet from an expanded state to a contracted state.

[0031] These and other aspects and embodiments of the disclosure are illustrated and described below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] The invention is described with reference to the following figures, which are presented for the purpose of illustration only and are not intended to be limiting.

[0033] In the Drawings:

[0034] Figure 1A illustrates phase transformation of the structure with an array of open holes of the same size; and the switching between two different variants in an elastomeric meta-structure with through-holes by applying pressure mechanically in the plane of the slab.

[0035] Figure 1B illustrates phase transformation of a structure with an array of isolated air pockets of alternating-sized illustrating the ability to both phase transform between the parent phase and the ferroelastic phase and switch between two different variants.

[0036] Figure 2 illustrates fabrication of the ferroelastic metamaterial. First, Ecoflex silicone resin is cast into a 3D printed mold to generate the desired structure. The elastomeric slab containing the array of holes was then removed from the mold. Two thin sheets of Ecoflex were used to cover the holes, and the structure glued and cured at reduced pressure (25 kPa).

When the completed structure was removed from the vacuum chamber, it underwent a phase transition from the parent phase to the ferroelastic phase.

[0037] Figures 3A-3D show phase transformation of the metamaterial in a vacuum chamber as external pressure decreases. **Figure 3A** shows the experimental images show the phase transformation from the ferroelastic phase to the parent phase. The scale bars are 2 cm long. **Figure 3B** shows simulation results of the same phase transition show a qualitative agreement with the experimental data. **Figure 3C** shows simulation results for the dependence of the total volume on the difference between the external and internal pressure, with the total volume V as an order parameter characterizing the phase transition. **Figure 3D** shows simulation results for the dependence of aspect ratio $Q=\left(a-b\right)/\left(a+b\right)$ on the pressure difference, where a and b are the length of the sample in the horizontal and vertical directions respectively.

[0038] Figures 4A-4B show switching of the metamaterial (Pext ≈ 100 kPa) from the vertical variant to the horizontal variant in the ferroelastic phase. **Figure 4A** shows the switching by applying a load in the long axis, the rectangle sample is able to switch between its two variants and leaving with a spontaneous deformation even after the removal of the load. **Figure 4B** shows the bulk stress-strain curve of the rectangle sample during switching recorded by Instron. The scale bars are 2-cm long.

[0039] Figures 5A-5B show simulation of switching behavior. **Figure 5A** shows the ferroelastic phase with horizontal variant was realized by applying an external pressure (state (1)). A vertical compressive stress σ was then added. After an intermediate state (state (2)), the vertical variant switched to the horizontal variant (state (3)). **Figure 5B** shows simulated relation of the compressive stress σ and the compressive strain ε of a unit cell during domain switching.

[0040] Figures 6A-6F show the metamaterial exhibit different domain patterns. **Figure 6A** shows a single domain structure. **Figure 6B** shows a two-domain structure with a horizontal domain boundary. **Figures 6C and 6D** show a three-domain structure with two horizontal boundaries. **Figure 6E** shows a two-domain structure with a 45-degree domain boundary. **Figure 6F** shows a three-domain structure with two 45-degree domain boundaries. Domain boundaries are marked with a dotted line. Scale bars are 2 cm long.

[0041] Figures 7A-7C show shape-memory effect in the metamaterial. **Figure 7A** shows a long piece of metamaterial was glued to a block of same elastomer (Ecoflex) to demonstrate the effect. By bending of the sample, the metamaterial was compressed, and forced into in its vertical variant. **Figure 7B** shows that when environmental pressure decreased, the metamaterial transformed from the ferroelastic phase into the parent phase, and the block returned to being straight. **Figure 7C** shows that when the environmental pressure was again raised, the material transitioned back into the ferroelastic phase. The restoring force in the elastomer block favored the horizontal variant. Scale bars are 2 cm long.

DETAILED DESCRIPTION

[0042] Functional "soft metamaterials" that undergo mechanical deformation under uniform external stimuli are described. Exemplary stimuli include a change in ambient pressure, salt concentration/osmotic pressure, temperature, PH, applied external electric field, or magnetic field, etc.

[0043] The term "metamaterials" is traditionally used in optics to describe materials that contain microscopic features with similar or smaller sizes compared to the wavelength of light involved. The materials are usually arranged in repeating patterns, often at micron or smaller scales that are smaller than the wavelengths of the phenomena they influence. Metamaterials derive their properties not from the properties of the base materials, but from

their designed structure. Their precise shape, geometry, size, orientation and arrangement give them their properties.

[0044] The term "metamaterial" is used herein to describe a structure that contains a sub-structure with feature sizes that are orders of magnitudes smaller than the bulk material itself, e.g., greater than 1 or greater than 2 orders of magnitude, but orders of magnitude larger than the molecular or atomic scale e.g., greater than 1, or greater than 2 orders of magnitude. In such macro-metamaterials, the bulk material behaves like a uniform structure, and only an average effect of the sub-structures manifest in bulk. In one or more embodiments, the unit cell of the repeating substructure that contains the features is on the order of millimeters.

[0045] In one or more embodiments, a soft metamaterial is provided. These soft metamaterials are made up of stretchable or flexible materials, which allow the overall bulk structure, e.g., soft metamaterial, to deform. In one or more embodiments, the soft metamaterial includes an elastomer.

[0046] In some embodiments, the sub-structures of these soft metamaterials form repeating units, similar to how unit cells are repeated in crystalline materials at the molecular or atomic level. In one or more embodiments, the substructures are flexible, stretchable or capable of deformation or collapse. In other embodiments, the sub-structure also contains hard components, which don't deform itself, but are connected to the stretchable or flexible components, enabling the entire structure to deform. The soft metamaterials change shape through interactions of the smaller scale meta-structure within itself. These interactions can resemble those between atoms and molecules in crystalline materials. This technique of reproducing atomic or molecular level material properties with meso-scale structural properties opens the door to engineering new soft materials with new properties and functions.

[0047] The substructure for the metamaterial can be varied depending on the external stimulus selected for the mechanical deformation.

[0048] In some embodiments, the soft metamaterial can be made of a soft elastomeric matrix and sealed air pockets embedded therein, which are arranged in a repeating pattern. In this case, ambient pressure can be used to control the volume of the air pockets: increasing the ambient pressure collapses the air pods, and decreasing the ambient pressure expands the air pods. As the air pockets expand and contract, the bulk material is subject to a mechanical deformation.

[0049] In some embodiments, the soft metamaterial can be made of a soft elastomeric matrix and hydrogel pellets, which are accessible to the surface of the bulk material so that water can be exchanged with the environment. In this case, the ambient salt concentration/osmotic pressure can be used to control the volume of the hydrogel pellets: increasing the ambient salt concentration/osmotic pressure results in an outflow of the water content from the hydrogel pellet. The hydrogel shrinks in size and the volume occupied by the hydrogen collapses. Decreasing the ambient salt concentration/osmotic pressure results in an inflow of the water into the hydrogel pellet, and expands them. The hydrogel pellets are coupled to the soft elastomeric matrix so that the expansion and contraction of the hydrogel pellet brings about a mechanical deformation of the bulk material. In certain embodiments, the hydrogel pellets are in a tensile state due to dehydration (the hydrogel pellet may be dehydrated or less hydrated), and the internal compressive forces arises from the transition of the hydrogel pellet from an expanded state to a contracted state. In addition, the hydrogel pellets can be flexible, stretchable or capable of deformation or collapse. In this way, osmotic pressure serves a similar function to ambient pressure in the previous example.

[0050] In some embodiments, the soft metamaterial is made of a soft elastomeric matrix and soft or solid pellets with a high coefficient of thermal expansion. In this case, the ambient temperature can be used to control the volume of the soft or solid pellets. Increasing the ambient temperature results in expansion of the pellets; decreasing the ambient temperature results in contraction of the pellets. The soft or solid pellets are coupled to the soft elastomeric matrix so that the expansion and contraction of the soft or solid pellet brings about a mechanical deformation of the bulk material.

[0051] By designing the shape and arrangement of the air pockets, pellets, etc. inside the soft metamaterial that respond to stimuli to generate forces that mechanically deform the bulk structure, different macroscopic effects can happen as a result of their change of volume. As used herein, the rearrangement of the substructures or unit cells in response to mechanical deformation is referred to as a phase change.

[0052] In one aspect, an engineered metamaterial capable of phase change is described, in which the phase change is regulated by a single thermodynamic variable. In one or more embodiments, phase transition is achieved using the pressure differential between internal void spaces and external pressure. Other stimuli are contemplated, such as salt concentration/osmotic pressure, temperature, PH, applied external electric field or magnetic field. Notably, phase change is accomplished without an external mechanical compression.

[0053] In one aspect, an elastic metamaterial also possesses shape-memory properties, which requires their ferroelastic phase to have spontaneous strains. Thus, unlike the structure developed by Boyce and Bertoldi, which has no spontaneous strains, the elastic material is capable of switching between two variants, or orientations.

[0054] In one embodiment, a soft metamaterial is prepared from an elastic material containing a regular array of holes or voids in an elastomeric body. The array of holes is

prepared using an alternating arrangement of holes of different sizes. The array of holes can be on the meso-scale or macro-scale. (The holes can be as on the micron scale or smaller, or as large as meter scale, e.g., millimetre or centimetre scale, but remains one, two, or more orders of magnitude smaller than the size of the bulk material.) In one or more embodiments, the holes or voids are isolated from the environment, so that a change in external pressure exerts a force on the body. For example, when the external pressure is greater than the internal pressure, the void space experiences a compression. Alternatively, when the external pressure is less than the internal pressure, the void space experiences an expansion. In one or more embodiments, the void spaces are at sub-atmospheric pressure.

[0055] In some embodiment, a soft metamaterial can mimic the mechanism of a one-way shape memory alloy. An exemplary shape memory material is shown in **Figure 1B.** The block elastic structure includes a slab of polymeric elastomer having a regular array of holes with two sizes that is sealed within a thin elastomeric membrane with a sub-atmospheric pressure inside. In this case, the soft metamaterial has an array of cylindrical sealed air pockets embedded in a slab of elastomer. In some embodiment, the air pockets have two sizes, and these two kinds of air pockets are arranged in a checkerboard pattern in the square array. In some sense this material mimics an A+X- crystalline lattice, in which A+ and X- have different radii. The holes collapse when exposed to atmospheric pressure tha tis greater than the internal pressue of the holes or cylinders (resting in the ferroelastic phase), and open under low external pressure that is less than the internal pressure of the holes or cylinders (transforming to the parent phase). This design makes it possible to apply compressive stress isotropically to the structure simply by changing the external pressure (using a pressure-controlled chamber).

[0056] In some embodiment, the air pockets are arranged close enough so that the they are able to collapse into slits upon increasing the ambient pressure. The repeating unit of an

undeformed material has a square shape originally. But as the cylindrical air pockets deforms into slits, the material shrinks and become rectangular. The long axis of the longer slits (that is slits that come from the larger air pockets) will also be the long axis of the now deformed material. This is illustrated in Variant I and Variant II of **Figure 1B**, in which the two long axes are in different directions for the two variants.

[0057] These holes can either stay open and form a square lattice, or be collapsed and skew the lattice into a rectangular shape, depending on the differential pressure between the atmosphere and the pressure sealed inside the holes. This change of geometry of the unit cells (square to rectangle) closely is analogous to the "parent phase" to "ferroelastic phase" transformation in ferroelastic materials (cubic to tetragonal); however, unlike conventional ferroelastic materials, the transformation is dependent on external pressure instead of temperature.

[0058] The analogy can be extended to switching between "variants"—the two rectangular skewed "variants" of this lattice of holes in an elastomer can be switched through a uniaxial compression (from tall rectangle to wide rectangle), in a process similar to that in which different microscopic variants of a ferroelastic material can be switched by external loading (between three different tetragonal unit cells). Similar behavior can be observed with other systems, such as hydrogel pellets, which are flexible, stretchable or capable of deformation or collapse.

[0059] The phase transition, switching of variants, and shape-memory characteristics in this system is shown, both in experiment and in simulation.

[0060] Figure 2 sketches the method used to fabricate the elastomeric structure capable of phase transformation and switching in one or more embodiments. In this example, the structures are fabricated by casting elastomers in a mold. The mold is designed using a

computer-aided design (CAD) software (Solidworks). Starting from the CAD files, a 3D printer (StrataSys Fortus 250mc) generated the masters in acrylonitrile butadiene styrene (ABS) plastic. Pouring Ecoflex prepolymer into the template and curing it at 20 °C for 12 hours generated an elastomeric slab with the designed pattern of holes. The slab is removed carefully from the mold. The mold did not require surface treatment to aid release of the cured Ecoflex, as this silicone polymer does not adhere to the ABS. The large and small holes in the structure had diameters of 5 mm and 3 mm respectively. The centers of all the holes formed a square lattice of unit length 5 mm. Two 1 mm-thick sheets of Ecoflex were glued to this slab to seal the holes. By using the same Ecoflex as glue, a homogenous body is formed. The entire structure was cured in a desiccator at a pressure of 25 kPa under 20 °C for 12 hours. After removing the fully cured material from the vacuum chamber, all the internal holes collapse due to the hydrostatic force applied by the atmosphere. The material then develops a spontaneous strain and enters the ferroelastic phase.

[0061] Figures 3A-3D show the experiment and simulation of the phase transition from the ferroelastic phase to the parent phase of a block of this metamaterial, as the external pressure decreases. In this experiment, the collapsed sample was placed in a vacuum chamber, and the pressure was slowly lowered; the changes in the structure of the slab was observed with changing pressure. Reducing the external air pressure induced a phase transition from the ferroelastic phase (rectangle shape) to the parent phase (square shape); raising the pressure inside the chamber resulted in a reversal of this transition (**Figure 3A**). Simulations were in good qualitative agreement with the experimental observations (**Figure 3B**).

[0062] The order of the phase transition can be determined by plotting the order parameter against the thermodynamic variable of this system—differential pressure $\Delta P = P_{\text{internal}} - P_{\text{external}}$. We choose the total volume of the slab V as an order parameter to characterize the phase

transition. With the increase of the difference between the external pressure and the internal pressure, the total volume V first decreases slowly and then drops sharply after a critical pressure difference (**Figure 3C**). The volume change is continuous at the critical pressure difference, but its derivative is not. This kink in the volume-pressure curve implies that the phase transition is second-order.

[0063] We can also define another order parameter $Q=(a-b)/(a+b)$ to differentiate the two variants of the ferroelastic phase. Value a and b are the length of the sample in the horizontal and vertical directions respectively. In the parent phase, this order parameter equals 0. At a critical pressure, a bifurcation occurs. Once in the ferroelastic phase, Q tends to 1 and -1 for the horizontal variant and the vertical variant respectively, as the pressure difference tends to infinity (**Figure 3D**).

[0064] In the ferroelastic phase, the metamaterial can switch from the vertical variant to the horizontal variant under a compressive load in the vertical direction (**Figures 4A-4B**. The switching occurs through a nucleation process in which one variant suddenly appears inside the other, forming domains of different variants, and seen at the 'domain wall' of **Figure 4A.** The formation of domains of different variants is accompanied by a "snap through" from one variant into the other. Then the horizontal domain expands and the vertical domain shrinks, while the domain wall moves. In the intermediate stages, the domain wall can be seen in the middle of the material. By the end, the domain wall disappears and the switching from the vertical variant to the horizontal variant is complete (**Figure 4A**). The new state remains stable even after removal of the compressive load, and left a spontaneous deformation. The phase state change occurs without transition through a stable parent phase. The bulk stress-strain curve of a rectangular sample during switching using an Instron is shown n **Figure 4B**, where (1), (2), (3), and (4), correspond to images in **Figure 4A**. The multiple nucleation

points can be seen as bumps in this plot. The original vertical domain can be regenerated by application of a compressive force in the direction orthogonal to that used to generate the horizontal domain.

[0065] The switching between variants using the finite element method is simulated, as shown in **Figures 5A** and **5B**). A simulated unit cell (the smallest repeating unit in our structure) can be placed in the ferroelastic phase (as opposed to the parent phase in a stress free state) by applying a hydrostatic differential pressure between the external boundary and the inside of the holes. When a vertical compressive stress is applied, the vertical variant switches to the horizontal variant (**Figure 5A**). **Figure 5B** plots the compressive stress σ as a function of the compressive strain ε of a unit cell. As the strain ε increased, the compressive stress σ first increased, then dropped below zero, and then increased again—this curve indicates that a "snap through" happens during the compression process. The results are consistent with the experiments.

[0066] The switching demonstrates that different variants can coexist under the ferroelastic phase. Furthermore, these different variants can divide a piece of material into domains of different shapes, and form domain boundaries (**Figures 6A-6F**). In the simplest case, the material can demonstrate a single crystal structure, if all parts of the structure are in the same variants in the ferroelastic phase, as shown in **Figure 6A**. The single-crystal structure can transform into a structure with two variants divided by a horizontal boundary under uniaxial loading, as shown in **Figure 6B**. More complicated loadings can lead to many more different domain patterns (See, e.g., **Figures 6C-6F**). These domain patterns are highly similar in ferromagnetic domain patterns, which are induced by ferromagnetic phase transitions.

[0067] **Figures 7A-7C** demonstrate the shape-memory effect of this metamaterial. A long piece of the metamaterial is glued to a horizontally positioned block made of same elastomer

(Ecoflex 00-30). Under high external pressure, the metamaterial transforms to the ferroelastic phase. The material was then bent manually. By bending of the sample, the metamaterial is compressed, and forced into in its vertical variant, as shown in **Figure 7A**. The material can be returned to its parent state by placing the bent composite sample into a vacuum chamber, and lowering the pressure. The decrease in environmental pressure induced a phase transition of the metamaterial from the ferroelastic phase back to the parent phase. Subsequently, the metamaterial returned to its initial length, and the curvature of the composite disappeared as shown in **Figure 7B**. When the environmental pressure was again raised, the material transitioned back into the ferroelastic phase. The storing force in the elastomer block favored the horizontal variant. Thus the majority of the material transformed into the horizontal variant instead of the vertical one, as shown in **Figure 7C**. This behavior is similar to that of one-way shape-memory alloys such as Nickel Titanium.

[0068] Meso-scale materials offer opportunities to control structure and properties beyond those in atomic and molecular materials. Although most of the familiar examples of phase transitions happen at the molecular or atomic scale, there are only a limited number of chemical elements (e.g. the atoms of the periodic table) that are available to form materials. There are an essentially unlimited number of options in the type of materials, geometry and interactions among which to choose, in generating new materials. Thus, more structures and functionalities are, in principle, possible using meso- or macro-scale materials than with atoms and molecules.

[0069] A metamaterial capable of phase transforming from the parent phase to the ferroelastic phase is described. This material exhibits a spontaneous strain and can be switched between its two different variants in the ferroelastic phase. These mechanisms are conceptually the same as those in a one-way shape-memory alloy, but happen in a very different length scale. The class of materials presented in this paper are useful, since they are "shape-memory

alloys" of arbitrarily low modulus and arbitrarily large remnant strain. This technique of reproducing atomic or molecular level material properties with meso scale structural properties opens the door to engineering new soft materials with new properties and functions.

[0070] The shape memory properties of these novel materials make them suitable for in a variety of fields, such as robotics. For example, the ability for the material to return to its initial shape makes is useful as an actuator in robotic applications.

[0071] Unless otherwise defined, used or characterized herein, terms that are used herein (including technical and scientific terms) are to be interpreted as having a meaning that is consistent with their accepted meaning in the context of the relevant art and are not to be interpreted in an idealized or overly formal sense unless expressly so defined herein. For example, if a particular composition is referenced, the composition may be substantially, though not perfectly pure, as practical and imperfect realities may apply; e.g., the potential presence of at least trace impurities (e.g., at less than 1 or 2%) can be understood as being within the scope of the description; likewise, if a particular shape is referenced, the shape is intended to include imperfect variations from ideal shapes, e.g., due to manufacturing tolerances. Percentages or concentrations expressed herein can represent either by weight or by volume.

[0072] Although the terms, first, second, third, etc., may be used herein to describe various elements, these elements are not to be limited by these terms. These terms are simply used to distinguish one element from another. Thus, a first element, discussed below, could be termed a second element without departing from the teachings of the exemplary embodiments. Spatially relative terms, such as "above," "below," "left," "right," "in front," "behind," and the like, may be used herein for ease of description to describe the relationship of one element to another element, as illustrated in the figures. It will be understood that the

spatially relative terms, as well as the illustrated configurations, are intended to encompass different orientations of the apparatus in use or operation in addition to the orientations described herein and depicted in the figures. For example, if the apparatus in the figures is turned over, elements described as "below" or "beneath" other elements or features would then be oriented "above" the other elements or features. Thus, the exemplary term, "above," may encompass both an orientation of above and below. The apparatus may be otherwise oriented (e.g., rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly. Further still, in this disclosure, when an element is referred to as being "on," "connected to," "coupled to," "in contact with," etc., another element, it may be directly on, connected to, coupled to, or in contact with the other element or intervening elements may be present unless otherwise specified.

[0073] The terminology used herein is for the purpose of describing particular embodiments and is not intended to be limiting of exemplary embodiments. As used herein, singular forms, such as "a" and "an," are intended to include the plural forms as well, unless the context indicates otherwise.

[0074] It will be appreciated that while a particular sequence of steps has been shown and described for purposes of explanation, the sequence may be varied in certain respects, or the steps may be combined, while still obtaining the desired configuration. Additionally, modifications to the disclosed embodiment and the invention as claimed are possible and within the scope of this disclosed invention.

Claims

1. A soft metamaterial, comprising:

a bulk elastic material having a substructure contained within the material, the substructure having a repeat unit of a size one or more orders of magnitude smaller than the bulk material, wherein the substructure is made of a material configured to be responsive to an external stimulus to induce a mechanical deformation of the bulk elastic material.

2. The soft metamaterial of claim 1, wherein the external stimulus is selected from the group consisting of a change in ambient pressure, salt concentration/osmotic pressure, temperature, PH, applied external electric field, mechanical pressure, hydrostatic pressure and magnetic field.

3. The soft metamaterial of claim 1, wherein the repeat unit has a size in the range of about 1 μm to about 1 m, or a repeat unit has a size in the range of about 1 μm to about 1 cm, or a repeat unit has a size in the range of about 1 μm to about 1 mm.

4. The soft metamaterial of claim 1, wherein the repeat unit has a size in the range of about 100 μm to 1 cm.

5. The soft metamaterial of claim 1, wherein the substructure comprises a regular array of sealed holes or voids in an elastomeric body and isolated from the environment.

6. The soft metamaterial of claim 5, wherein the array of holes or voids comprises an alternating arrangement of larger and smaller holes or voids.

7. The soft metamaterial of claim 5, wherein the internal pressure inside the array of holes or voids is at a sub-atmospheric pressure.

8. The soft metamaterial of claim 7, wherein the array of holes or voids are in an expanded state when the external pressure matches the sub-atmospheric pressure of the holes or voids and in a collapsed state when the external pressure is greater than the sub-atmospheric pressure of the of holes or voids.

9. The soft metamaterial of claim 1, wherein the substructure comprises a regular array of hydrogel pellets, wherein the hydrogel pellets are in communication with the environment and/or with one another.

10. The soft metamaterial of claim 9, wherein the hydrogel pellets are in a resting expanded state when the environment is at a first condition that forms a hydrated hydrogel pellet and in a collapsed state when the environment is at a second condition that form a dehydrated or less hydrated hydrogel pellet.

11. The soft metamaterial of claim 10, wherein the first and/or second condition is selected from the group consisting of salt concentration/osmotic pressure, temperature, PH, and applied external electric field.

12. The soft metamaterial of claim 9, wherein the array of hydrogel pellets comprises an alternating arrangement of larger and smaller hydrogel pellets.

13. The soft metamaterial of claim 1, wherein the substructure comprises an array of soft pellets with a high degree of thermal expansion.

14. The soft metamaterial of claim 13, wherein the array of soft pellets comprises an alternating arrangement of larger and smaller soft pellets.

15. The soft metamaterial of claim 13, wherein the soft pellets are in an expanded state at a first higher temperature and in a collapsed state at a second lower temperature.

16. A method of deforming a bulk material, comprising:

providing a soft metamaterial, comprising an elastic material having a substructure contained within the material, the substructure having a repeat unit of size one or more orders of magnitude smaller than the bulk material, wherein the substructure is made of a material that is responsive to an external stimulus, and

exposing the soft metamaterial to an external stimulus, wherein a response of the substructure to an external stimulus induces a mechanical deformation of the bulk elastic material.

17. The method of claim 16, wherein the external stimulus is selected from the group consisting of a change in ambient pressure, salt concentration/osmotic pressure, temperature, PH, applied external electric field and magnetic field.

18. The method of claim 16, wherein the substructure is selected from the group consisting of sealed air pockets, hydrogel pellets and solid thermally expanding solid pellets.

19. The method of claim 16, wherein the substructure comprises an array of holes having an internal pressure, wherein the holes are in an expanded state when the external pressure matches the internal pressure of the of holes and in a collapsed state when the external pressure is greater than the internal pressure of the of holes; and the method comprises

changing the external pressure to induce a phase change from the expanded state to the collapsed state (or vice versa) in the material.

20. A method of inducing a phase change in a material comprising:

providing a bulk elastic material having a substructure contained within the material, the substructure having a repeat unit of a size one or more orders of magnitude smaller

than the bulk material, wherein the substructure comprises an alternating arrangement of larger and smaller compressible elements, wherein the bulk elastic material is capable of taking on two different orientations when the bulk elastic material is under an internally generated compression; and

applying a first external force to the bulk elastic material, wherein the material switches between orientations.

21. A method of inducing a phase change in a material comprising:

providing a bulk elastic material having a substructure contained within the material, the substructure having a repeat unit of a size one or more orders of magnitude smaller than the bulk material, wherein the substructure comprises an array of holes having an alternating arrangement of larger and smaller holes, the hole maintained at a pressure less than the ambient pressure, wherein the bulk elastic material is capable of taking on two different orientations when the bulk elastic material is under ambient pressure; and

applying a first external force to the bulk elastic material, wherein the material switches between orientations.

22. The method of claim 20 or 21, wherein the bulk elastic material retains the new orientation after release of the first applied external force.

23. The method of claim 22, wherein the bulk elastic material reverts to the initial orientation upon application of a force perpendicular to the first applied external force.

24. The method of claim 20, wherein the compressible elements comprise hydrogel pellets which are in a tensile state due to dehydration, and the internal compressive

forces arises from the transition of the hydrogel pellet from an expanded state to a contracted state.

Figure 1A

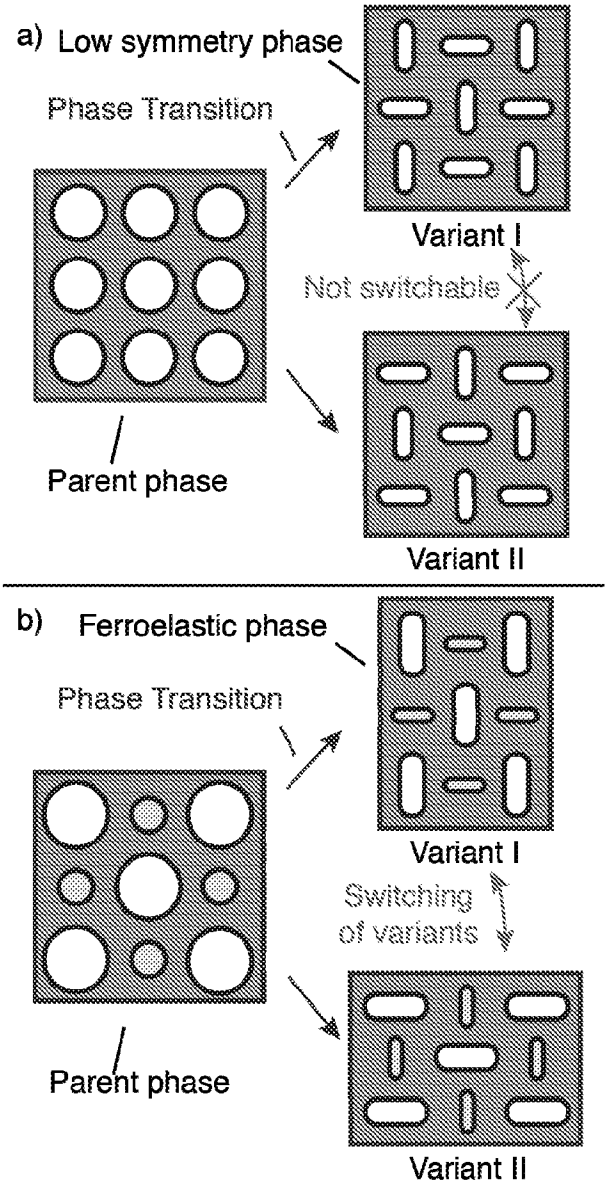

Figure 1B

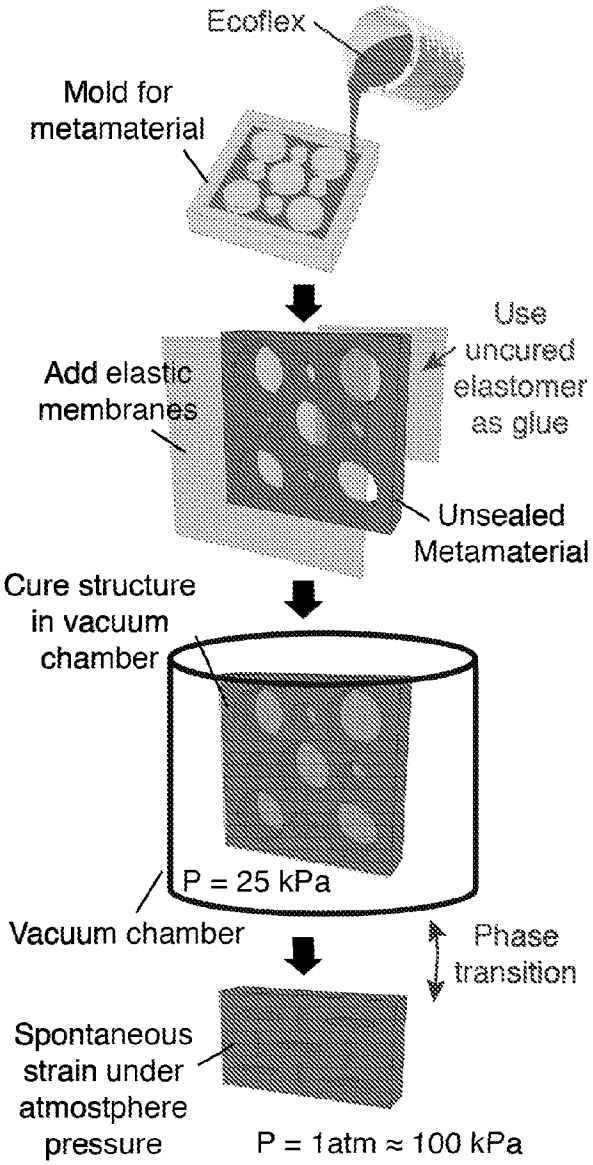
Ecoflex
Mold for metamaterial
Use uncured elastomer as glue
Add elastic membranes
Unsealed Metamaterial
Cure structure in vacuum chamber
P = 25 kPa
Vacuum chamber
Phase transition
Spontaneous strain under atmostphere pressure
P = 1atm ≈ 100 kPa

Figure 2

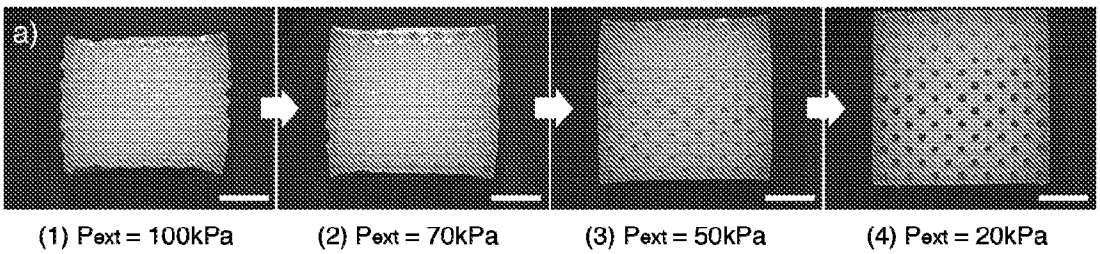

Figure 3A

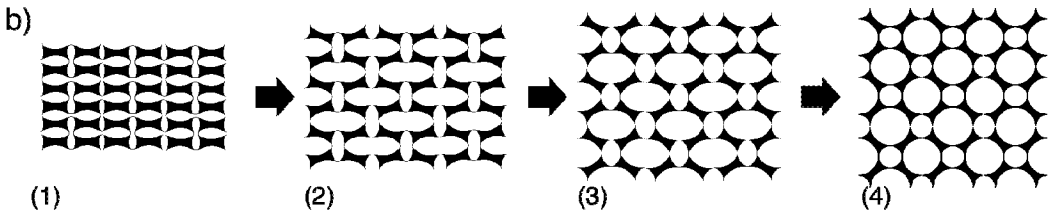

Figure 3B

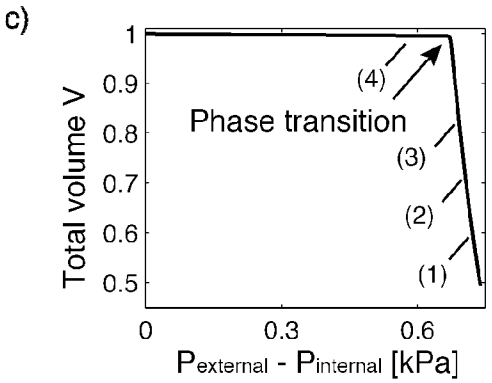

Figure 3C

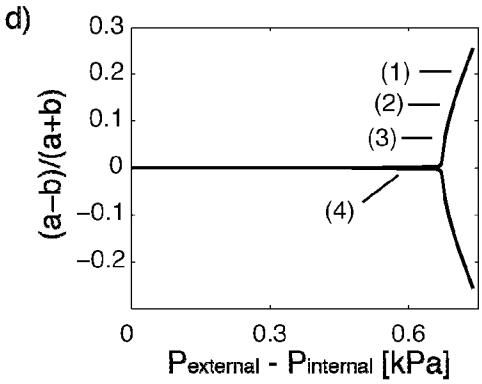

Figure 3D

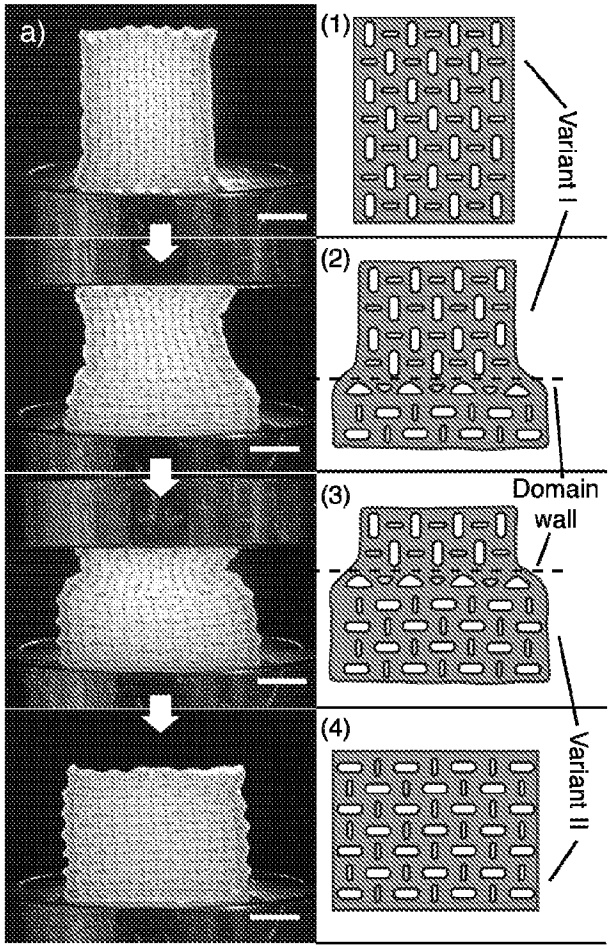

Figure 4A

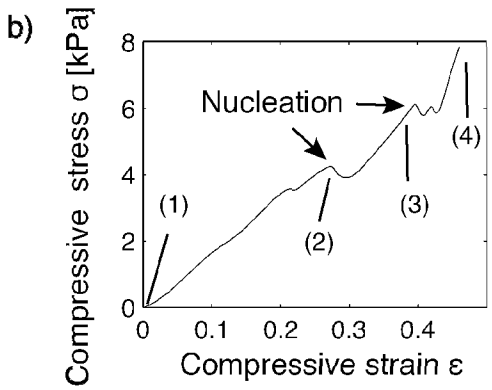

Figure 4B

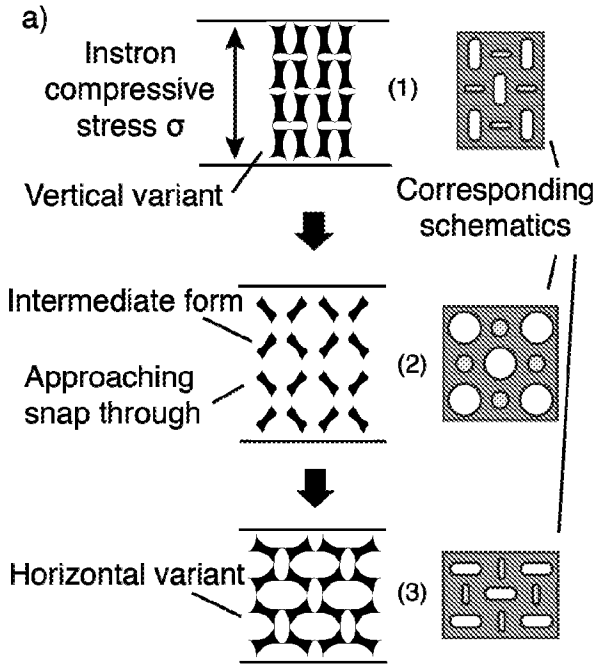

Figure 5A

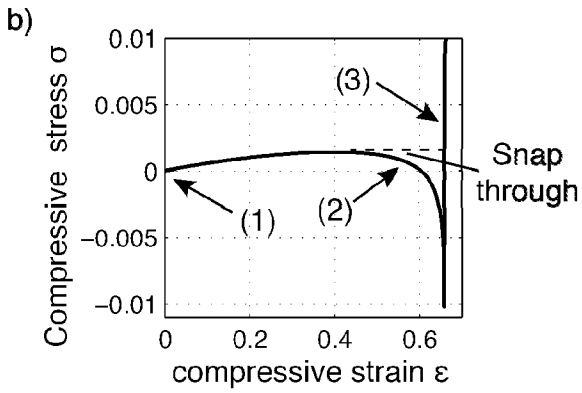

Figure 5B

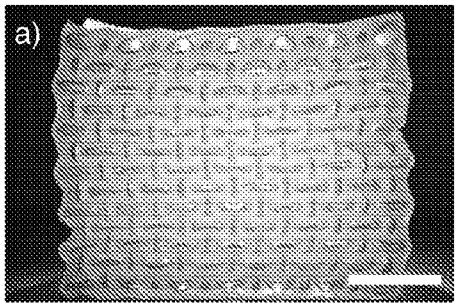

Figure 6A

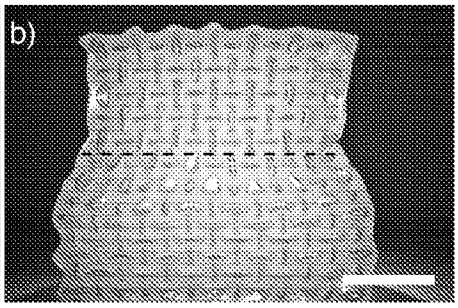

Figure 6B

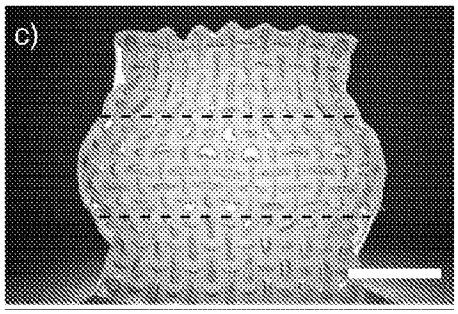

Figure 6C

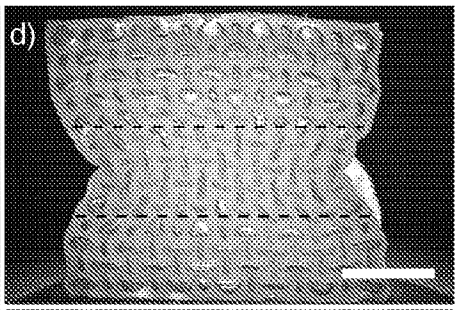

Figure 6D

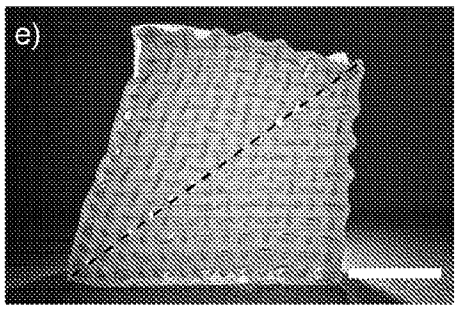

Figure 6E

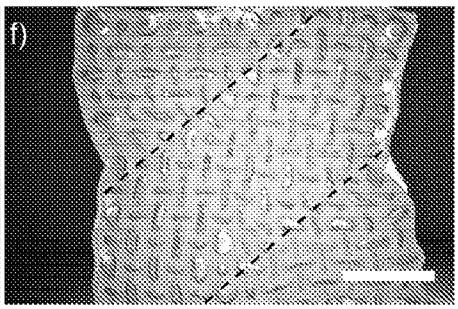

Figure 6F

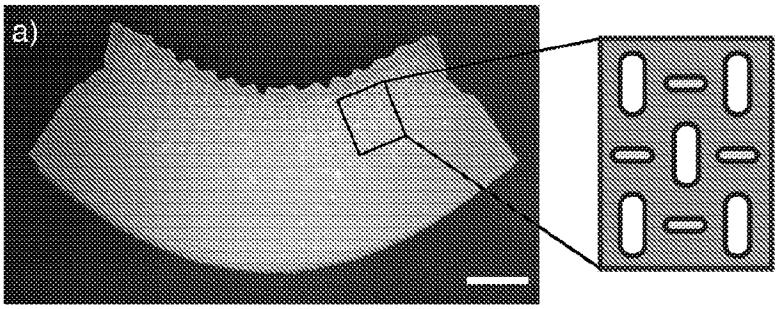

Figure 7A

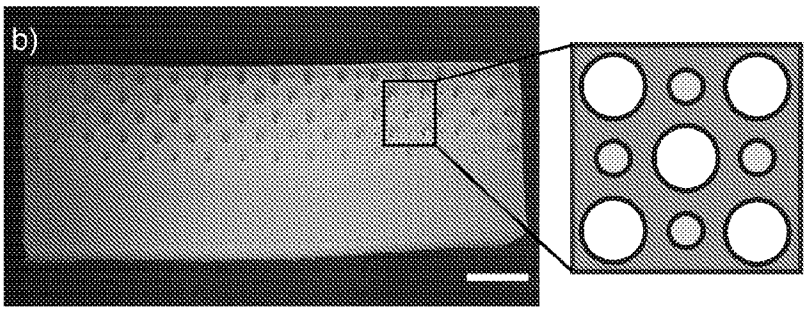

Figure 7B

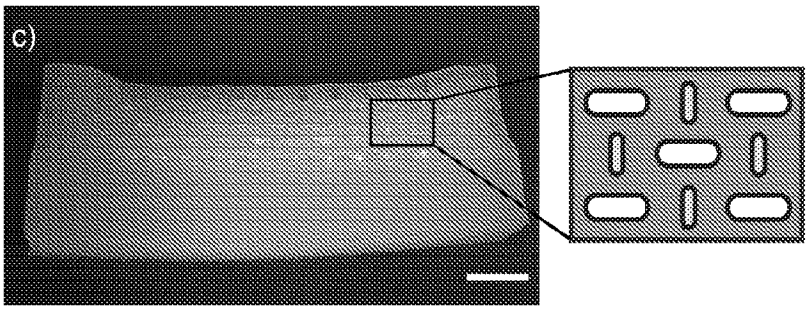

Figure 7C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/45107

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08F 291/02; C08K 5/5419 (2016.01)
CPC - C08F 291/02; C08K 5/5419
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): C08F 291/02; C08K 5/5419 (2016.01)
CPC: C08F 291/02; C08K 5/5419

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 524/266; 524/502 (key word limited; see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar
Search terms used: soft metamaterials, elastomeric, phase changing/transforming, shape memory, ferroelastic, external stimuli

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	WO 2015/109359 A1 (RMIT UNIVERSITY) 30 July 2015 (30.07.2015); para [001], [020], [034]-[035], [044], [048], [064]-[065], [068], [117], [119], [123]-[124], [150], [154], [172]; Figs. 1, 4, 6	1-5, 7-8, 16-19 ---------- 6, 9-15, 20-24
Y	FLORIJN B. et al., "Programmable Mechanical Metamaterials", Physical Review Letters [online], 24 October 2014 , Vol.113, issue 17, article number 175503, pages 1-5; retrieved from the Internet: <DOI: 10.1103/PhysRevLett.113.175503>; see entire document, especially pg. 1-3; Figs. 1 and 3	6, 12, 14, 20-24
Y	US 2002/0176880 A1 (CRUISE et al.) 28 November 2002 (28.11.2002); para [0004], [0006], [0008], [0011], [0031]-]0033], [0040]-[0041]	9-15, 24

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 September 2016 (20.09.2016)	21 OCT 2016

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)