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Phase-transforming and switchable metamaterials

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ABSTRACT

This paper demonstrates a new soft structure that uses a meso- or macro-scale elastic instability to generate a shape-memory effect similar to that exhibited by a ferroelastic material. It demonstrates the phase transitions, state switching, and shape-memory effects in this system, both in experiment and in simulation. The new class of materials described in the paper is potentially useful, since it comprises what are effectively "shape-memory alloys" of arbitrarily low modulus and arbitrarily large remnant strain. The reproduction of properties of materials usually associated with atomic- or molecular-level changes in structure using meso-scale structural opens the door to development of new, soft materials with new properties and functions.

1. Introduction

Many forms of matter – atoms, ions, 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 are 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 [1], smectic-A to nematic transition in liquid crystals [2], 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 of materials exhibiting second-order phase transitions are ferroelectric [3–5] and ferromagnetic materials [6], shape memory alloys [7], ferroelastic materials [8–10], superconductors [11], and superfluids [12]. A similar definition could be applied to higher-order phase transitions.

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 macro-scale include colloidal suspensions [13,14], 2D arrays of polymeric spheres [15], heat-shrinkable polymer patterns [16], meso-scale silicon rods embedded in a hydrogel [17–19], and slabs of elastomer with an array of holes [20–23]. 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 and voids filled with gas or liquids

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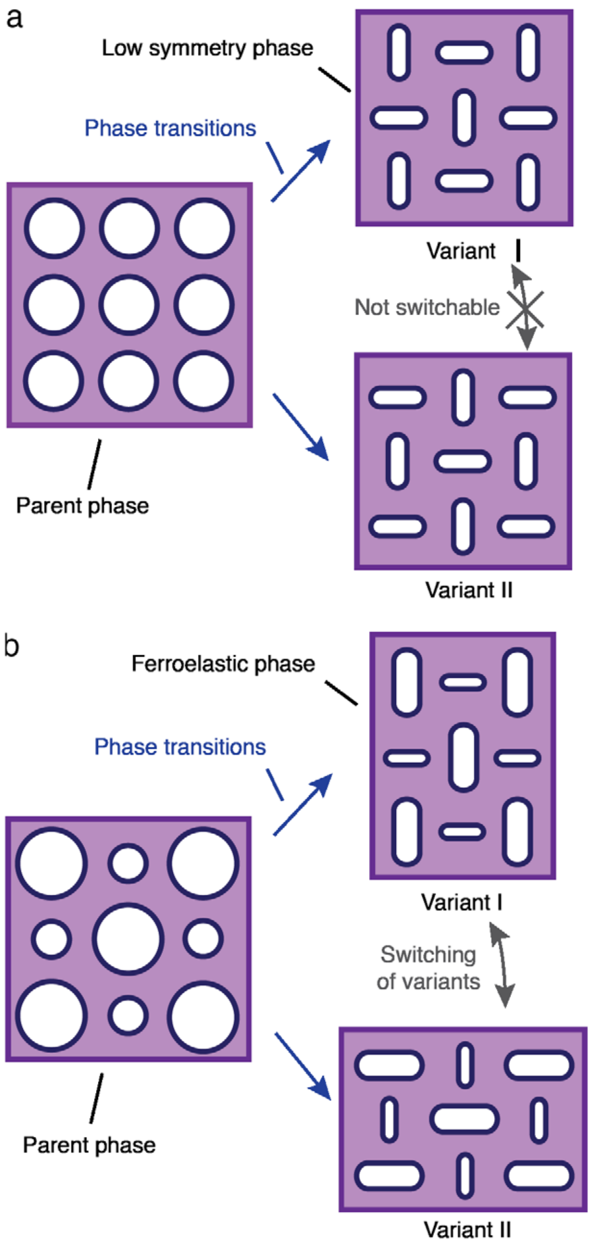

Fig. 1. Change of phases and switching between variants. (a) For an elastomeric block containing holes of the same size, the parent phase transforms to a low-symmetry phase. In the low-symmetry phase, the structure has two variants of the same state of spontaneous strain, so that one variant cannot be switched to the other under external force. (b) For an elastomeric block containing holes of different sizes, the parent phase transforms to a ferroelectric phase. In the ferroelectric phase, the structure has two variants of different states of spontaneous strain, so that one variant can be switched to the other variant by an external mechanical force.

– through geometry and mechanics, at meso- or macro-scale. This letter describes 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.

Ferroelasticity is the mechanical analogue of ferroelectricity and ferromagnetism, and it is the mechanism that underlies the characteristics of shape-memory alloys [24]. When cooled below a certain temperature – the "Curie temperature" – a ferroelastic material undergoes a phase transition, develops spontaneous strains, and is said to be in a "ferroelastic phase". These microscopic states of spontaneous strain – also known as "variants" – are equivalent crystal structures in different orientations (e.g. 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 heated above the Curie temperature, 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 (e.g. the tetragonal unit cells become cubic). As a result, the material returns to its original shape, and thus generates a shape-memory effect.

Our design is motivated by a structure made of a block of elastomer with an array of through-holes having the same sizes, which is able to realize a macroscopic "phase change" (i.e., a change in stress–strain properties when the material is compressed beyond a certain threshold) by applying pressure mechanically in the plane of the slab [20,21]. Bertoldi et al. explored this type of structure as a negative Poisson ratio material [25] and a tunable phononic crystal [26], while Yang et al. demonstrated other related examples [27]. We wished to engineer a material whose change of phases is regulated by an environmental stimulus (such as temperature, or atmospheric pressure), instead of an applied mechanical compression. We also wished to engineer the elastic meta-material to possess shape-memory properties; for these properties to exist, the material must have a spontaneous strain. The structure developed by Boyce and Bertoldi will phase transform, but since the two variants of their low-symmetry phase have the same state of spontaneous strain, it is difficult to switch between them using an external mechanical force (Fig. 1(a)). That is, these structures are not ferroelastic and cannot realize shape memory.

We developed an elastic structure comprising a slab of elastomer having a regular array of holes with two sizes that are sealed within a thin elastomeric membrane with a sub-atmospheric pressure inside the holes (Fig. 1(b)). (In some sense this material mimics an A^+X^- crystalline lattice, in which A^+ and X^- have different radii.) These holes can either stay open and form a square lattice, or collapse and skew the lattice into a rectangular shape, depending on the differential pressure between the atmosphere outside and the pressure inside the sealed holes. This design made it possible to apply compressive stress isotropically to the structure simply by changing the external pressure (using a pressure-controlled chamber).

Having holes of two different sizes enable the block to collapse – when the external pressure is above a critical level – into two distinct states of spontaneous strain, which we call the "vertical" and "horizontal" variants, respectively (depending on whether the direction of the spontaneous strain is vertical or horizontal). This change of shape of the unit cells (square to rectangle) closely resembles the transformation of "parent phase" to "ferroelastic phase" in ferroelastic materials (cubic to tetragonal), but is dependent on external pressure instead of temperature. The analogy can be extended to switching of "variants", as 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). We demonstrate the phase transition, state switching, and shape-memory effects in this system both in experiment and in simulation.

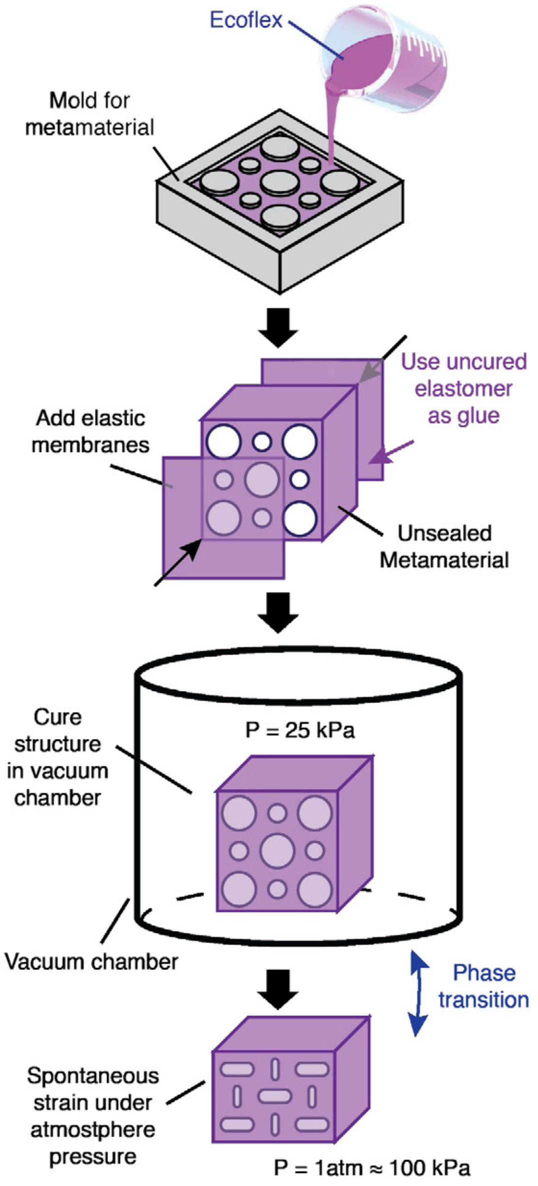

Fig. 2. Fabrication of the ferroelastic metamaterial. First, we cast Ecoflex into a 3D printed mold to generate the desired structure. The elastomeric slab containing the array of holes was then removed from the mold. Two thin sheets of Ecoflex were used to cover the holes, and the structure glued and 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.

2. Results and discussion

Fig. 2 sketches the method we used to fabricate an elastomeric structure capable of phase transition and state switching. These structures are fabricated by casting elastomers in a mold. We designed the mold using 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 masters and curing it at 20 °C for 12 h generated an elastomeric slab

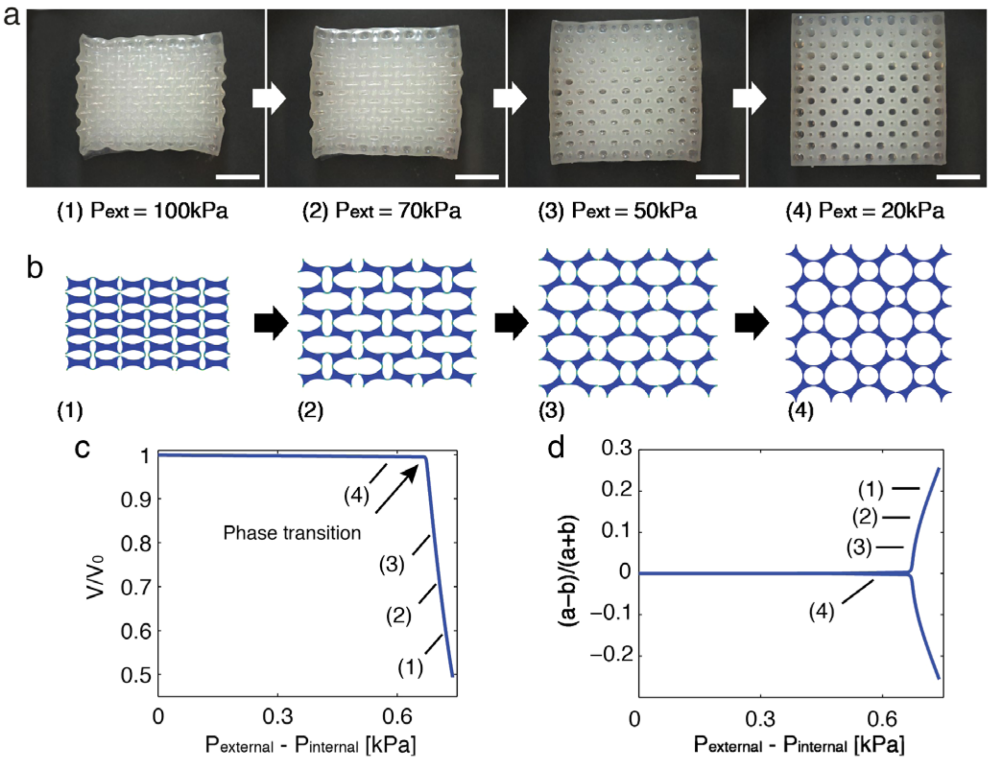

Fig. 3. Phase transition of the metamaterial as the external pressure decreases. (a) The experimental images show the phase transition from the ferroelastic phase to the parent phase. The scale bars are 2 cm long. (b) Simulation results of the same phase transition show a qualitative agreement with the experimental data. (c) Simulation results for the dependence of the total volume on the difference between the external and internal pressure, with the normalized total volume V/V_0 as an order parameter characterizing the phase transition. (d) Simulation results for the dependence of aspect ratio $Q = (a - b)/(a + b)$ on the pressure difference, where a and b are the length of the bulk sample in the horizontal and vertical directions respectively.

with the designed pattern of holes. We then removed the slab carefully from the mold. The mold did not require any surface treatment to promote the release of the cured Ecoflex, as this silicone polymer does not adhere to 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. We subsequently glued two 1 mm-thick sheets of Ecoflex to this slab (30 mm thick) to seal the holes. We used the same Ecoflex as glue, and cured the entire structure in a vacuum chamber at a pressure of 25 kPa under 20 °C for 12 h. After removing the fully cured material from the vacuum chamber, all the internal holes collapse due to the hydrostatic force applied by the atmosphere. When exposed to atmospheric pressure, the material develops a spontaneous strain and enters the ferroelastic phase.

Fig. 3 shows 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 our experiment, we put the collapsed sample in a vacuum chamber, lowered the pressure, and observed the structure of the slab. 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 (Fig. 3(a), supporting videos: Phase transition square.mp4, Phase transition diamond.mp4).

We also used finite element method to simulate the phase transition of the metamaterial with holes of two different sizes in a plane strain condition. We simulated a unit cell of the metamaterial. We used the neo-Hookean model with shear modulus $G = 30$ kPa for the material. In the experiment, the air pressure inside the holes increases as the volume of the holes decreases, which has a stabilizing effect to the phase transition. To simplify the simulation, we did not consider the effect of air. To compensate this effect and obtain a second-order phase transition, we simulated the metamaterial with holes of slightly different sizes: 6 mm and 3.5 mm respectively. Simulation results were in good qualitative agreement with the experimental observations (Fig. 3(b)).

The order of the phase transition can be determined by plotting the simulated values of the order parameter against the thermodynamic variable of this system—differential pressure $\Delta P = P_{\text{external}} - P_{\text{internal}}$. We choose the ratio of the total volume of the slab in the current state V to the volume of the stress free state V_0, V/V_0 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 the critical differential pressure $\Delta P = 0.672$ kPa is reached (Fig. 3(c)). The volume change is continuous at the critical pressure difference, but its derivative is not. This kink in

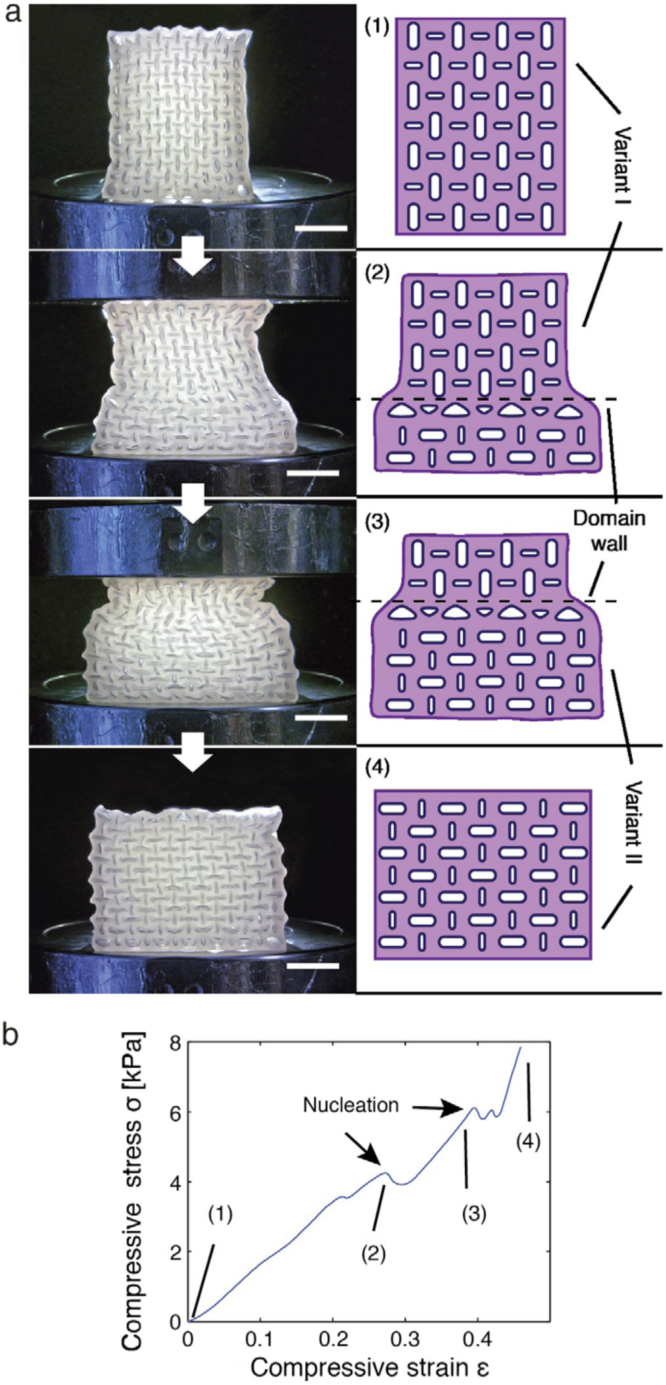

Fig. 4. Switching of the metamaterial (under atmospheric pressure) from the vertical variant to the horizontal variant in the ferroelastic phase on vertical compression. (a) By applying a compressive load in the long axis, the rectangular sample switches between its two variants. The spontaneous strain persists even after the removal of the load. (b) The bulk stress–strain curve of the rectangular sample during switching as recorded by Instron. The scale bars are 2 cm long.

the volume–pressure curve is a signature of a second-order phase transition.

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 bulk sample in the horizontal and vertical directions, respectively. This order parameter naturally captures the breaking of symmetry in the phase transition. In the parent phase, $Q = 0$. At a critical pressure (0.672 kPa, in our simulation), a bifurcation occurs, while the material enters the ferroelastic phase. Once in the ferroelastic phase, Q tends to 1 and -1 for the horizontal variant and the vertical

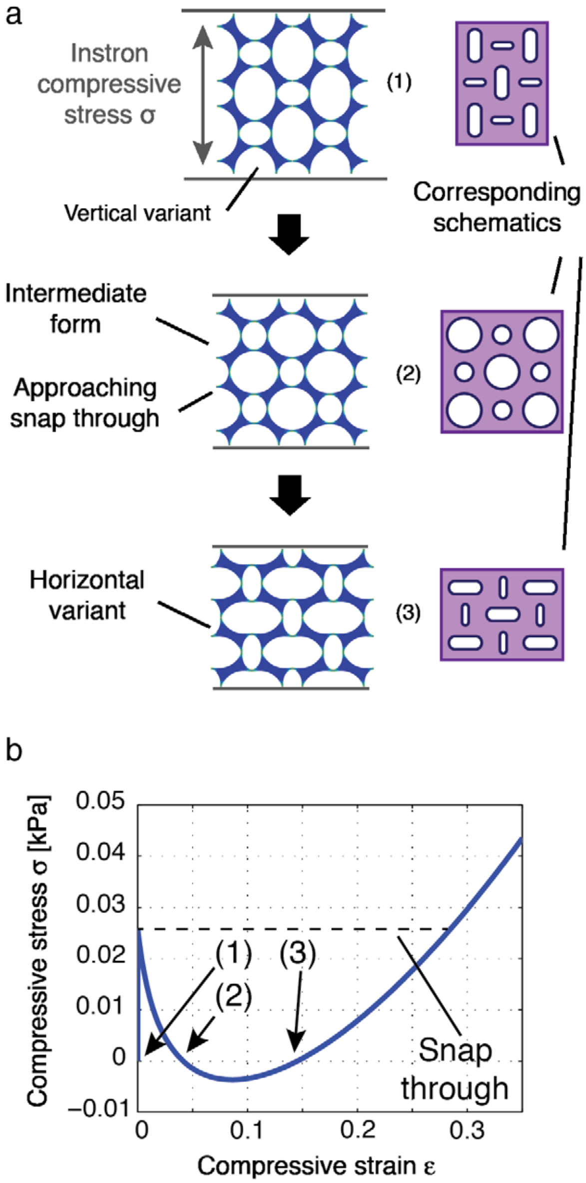

Fig. 5. Simulation of the switching behavior. (a) The ferroelastic phase in horizontal variant was realized by applying an external pressure (state (1)). A vertical compressive stress σ was then added. After an intermediate state (state (2)), the vertical variant switched to the horizontal variant (state (3)). (b) Simulated relation of the compressive stress σ and the compressive strain ε of a unit cell during domain switching.

variant respectively, as the pressure difference tends to infinity (Fig. 3(d)).

In the ferroelastic phase, the metamaterial can switch from the vertical variant to the horizontal variant under a compressive load in the vertical direction (Fig. 4). The switching initiates through a nucleation process in which one variant suddenly appears inside the other, forming domains of different variants; this nucleation is accompanied by a "snap through" [28–30]. The horizontal domain then expands and the vertical domain shrinks, while the domain wall moves upwards (supporting videos: Linear domain motion_1.mp4, Linear domain motion_2.mp4). 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 (Fig. 4(a)). The block results in a state of a spontaneous strain in the horizontal variant. The new state remains stable even after removal of the compressive load. We recorded the bulk stress–strain curve of a rectangular sample during switching using an Instron (Fig. 4(b)). The multiple nucleation points can be seen as bumps in this plot.

We simulated the switching between variants using the finite element method (Fig. 5). We first put a simulated unit cell (the smallest repeating unit in our structure) into 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

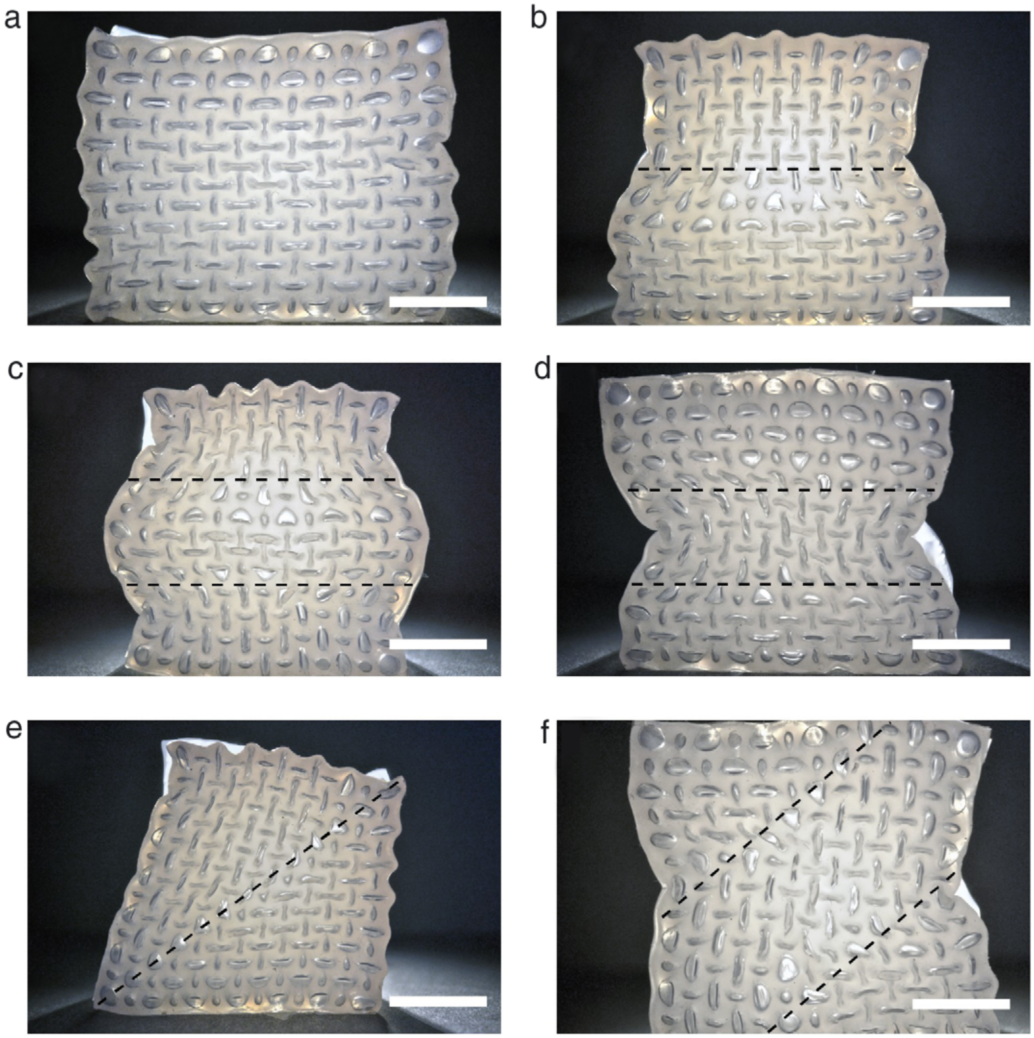

Fig. 6. Ferroelastic domain patterns. (a) A single-domain structure. (b) A two-domain structure with a horizontal domain boundary. (c, d) A three-domain structure with two horizontal boundaries. (e) A two-domain structure with a 45-degree domain boundary. (f) A three-domain structure with two 45-degree domain boundaries. Domain boundaries are marked with a dotted line. Scale bars are 2 cm long.

the holes $\Delta P = 0.685$ kPa. We further applied a compressive displacement in the vertical direction to switch the vertical variant to the horizontal variant (Fig. 5(a)), and recorded the corresponding stress. A small numerical stabilization was applied during the simulation of switching. We also noticed that in the experiments, the switching did not happen for all unit cells simultaneously, but through the accommodation of neighboring ones. Ideally, a simulation with more unit cells is needed to better capture the propagation of domains in the switching process. Here we used a simple simulation of a unit cell to demonstrate onset of the switching process. Fig. 5(b) plots the compressive stress σ as a function of the compressive strain ε of a unit cell with the ferroelastic state before the stretch as the reference. As the strain ε increased, the stress σ first increased, then dropped below zero, and then increased again—this curve indicates that a "snap through" happens during the compression process [28–30]. The results are consistent with the experiments.

The switching demonstrates that different variants can coexist. Furthermore, these different variants can divide a piece of material into domains of different shapes, and form domain boundaries (Fig. 6). 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 (Fig. 6(a)). The single-crystal structure can transform into a structure with two variants divided by a horizontal boundary under uniaxial loading (Fig. 6(b)). More complicated loadings can lead to many more different domain patterns (Fig. 6(c)–(f)). These domain patterns are highly similar to ferromagnetic domain patterns, which are induced by ferromagnetic phase transitions.

Fig. 7 demonstrates the shape-memory effect characteristic of this metamaterial. A long piece of the metamaterial is glued to a horizontally positioned block made of the same elastomer (Ecoflex). Under high external pressure, the metamaterial transforms to the ferroelastic phase.

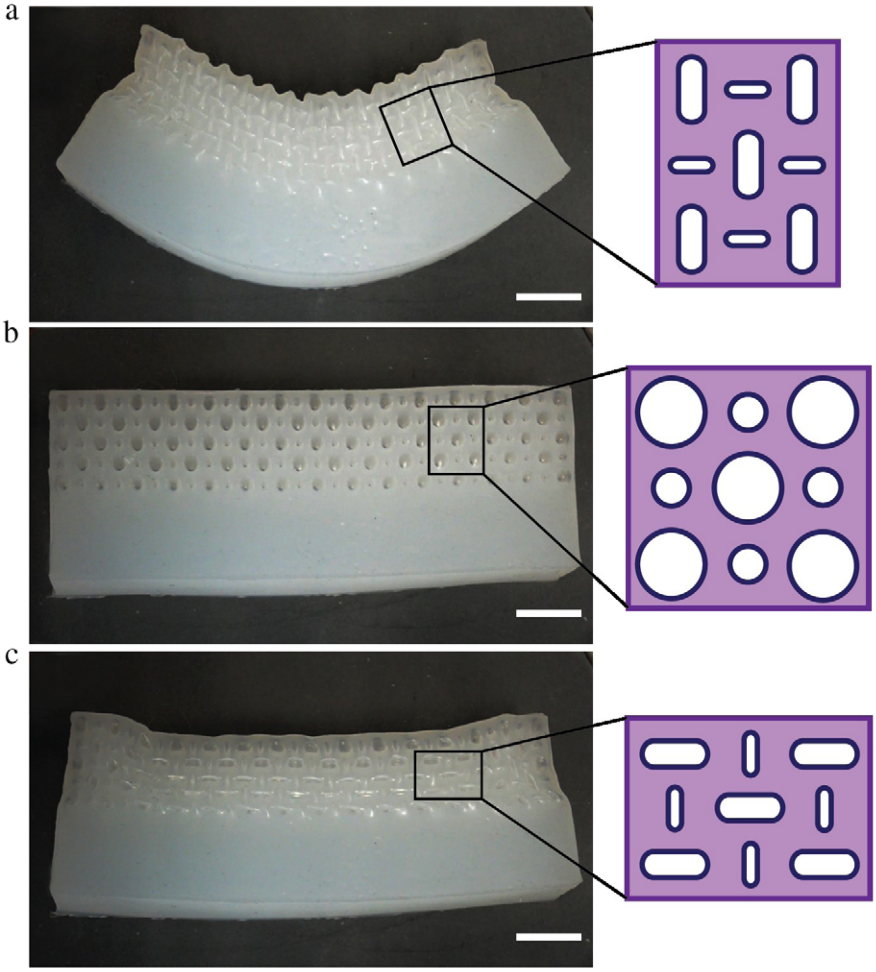

Fig. 7. Shape-memory effect in the metamaterial. (a) A long piece of metamaterial was glued to a block of the same elastomer (Ecoflex). When the metamaterial is in a ferroelastic phase under a high external pressure, by bending of the sample, the metamaterial was compressed, and forced into its vertical variant. (b) When the environmental pressure decreased, the metamaterial transformed from the ferroelastic phase into the parent phase, and the block returned to being straight. (c) When the environmental pressure was again raised, the material transformed back into the ferroelastic phase. The restoring force in the elastomer block favored the horizontal variant. Scale bars are 2 cm long.

After bending the metamaterial manually, the compression forces the system into its vertical variant (Fig. 7(a)). We then put the bent composite sample into a vacuum chamber, and lowered the pressure. The decrease in environmental pressure induced a phase transition of the metamaterial from the ferroelastic phase back to the parent phase (Supporting video: Shape memory.mp4). Subsequently, the metamaterial returned to its initial length, and the curvature of the composite disappeared (Fig. 7(b)). 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. Thus the majority of the material transformed into the horizontal variant instead of the vertical one (Fig. 7(c)). This behavior is similar to that of one-way shape-memory alloys such as Nickel Titanium.

3. Conclusions

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 involve structural transformations occurring 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 metamaterials. Thus, more structures and functionalities are, in principle, possible using meso- or macro-scale materials than with atoms and molecules.

We have created a metamaterial capable of phase transforming from a parent phase to a ferroelastic phase by a change in environmental pressure. In the ferroelastic phase, this material exhibits two variants of spontaneous strain, and one variant can be switched to the other under an external mechanical force. These mechanisms are conceptually the same as those in a one-way shape-memory alloy, but happen at a very different length scale.

The class of materials presented in this paper is potentially 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.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.eml.2015.11.004.

References

[1] D.A. Porter, K.E. Easterling, M. Sherif, Phase Transformations in Metals and Alloys, CRC Press, Boca Raton, 2011.
[2] B. Halperin, T. Lubensky, S.-k. Ma, Phys. Rev. Lett. 32 (1974) 292.
[3] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Oxford University Press, Oxford, UK, 1977.
[4] J.A. Gonzalo, B. Jiménez, Ferroelectricity: the Fundamentals Collection, John Wiley & Sons, 2008.
[5] H. Das, A.L. Wysocki, Y. Geng, W. Wu, C.J. Fennie, Nature Commun. 5 (2014) 2998.
[6] W. Dürr, M. Taborelli, O. Paul, R. Germar, W. Gudat, D. Pescia, M. Landolt, Phys. Rev. Lett. 62 (1989) 206.
[7] K. Guda Vishnu, A. Strachan, J. Appl. Phys. 113 (2013) 103503.
[8] E.K. Salje, Annu. Rev. Mater. Sci. 42 (2012) 265.
[9] T. Klatt, M.R. Haberman, J. Appl. Phys. 114 (2013) 033503.
[10] R.S. Elliott, N. Triantafyllidis, J.A. Shaw, J. Mech. Phys. Solids 59 (2011) 216.
[11] P. Townsend, J. Sutton, Phys. Rev. 128 (1962) 591.
[12] M.W. Zwierlein, J.R. Abo-Shaeer, A. Schirotzek, C.H. Schunck, W. Ketterle, Nature 435 (2005) 1047.
[13] P. Schall, I. Cohen, D.A. Weitz, F. Spaepen, Science 305 (2004) 1944.
[14] P. Schall, I. Cohen, D.A. Weitz, F. Spaepen, Nature 440 (2006) 319.
[15] B.A. Grzybowski, A. Winkleman, J.A. Wiles, Y. Brumer, G.M. Whitesides, Nature Mater. 2 (2003) 241.
[16] Q. Zhang, D. Yan, K. Zhang, G. Hu, Sci. Rep. 5 (2015) 8936.
[17] A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, J. Aizenberg, Science 315 (2007) 487.
[18] L.D. Zarzar, Q. Liu, X. He, Y. Hu, Z. Suo, J. Aizenberg, Soft Matter 8 (2012) 8289.
[19] W. Hong, X. Zhao, Z. Suo, J. Appl. Phys. 104 (2008) 084905.
[20] T. Mullin, S. Deschanel, K. Bertoldi, M. Boyce, Phys. Rev. Lett. 99 (2007) 084301.
[21] K. Bertoldi, M. Boyce, S. Deschanel, S. Prange, T. Mullin, J. Mech. Phys. Solids 56 (2008) 2642.
[22] B. Florijn, C. Coulais, M. van Hecke, Phys. Rev. Lett. 113 (2014) 175503.
[23] D. Restrepoa, N.D. Mankameb, P.D. Zavattieri, Extreme Mech. Lett. 4 (2015) 52.
[24] K. Otsuka, C.M. Wayman, Shape Memory Materials, Cambridge University Press, Cambridge, UK, 1999.
[25] K. Bertoldi, P.M. Reis, S. Willshaw, T. Mullin, Adv. Mater. 22 (2010) 361.
[26] P. Wang, J. Shim, K. Bertoldi, Phys. Rev. B 88 (2013) 014304.
[27] J. Li, J. Shim, J. Deng, J.T. Overvelde, X. Zhu, K. Bertoldi, S. Yang, Soft Matter 8 (2012) 10322.
[28] Z.P. Bažant, L. Cedolin, Stability of Structures: Elastic, Inelastic, Fracture and Damage Theories, World Scientific, Singapore, 2010.
[29] J. Zhu, T. Li, S. Cai, Z. Suo, J. Adhes. 87 (2011) 466.
[30] C. Keplinger, T. Li, R. Baumgartner, Z. Suo, S. Bauer, Soft Matter 8 (2012) 285.