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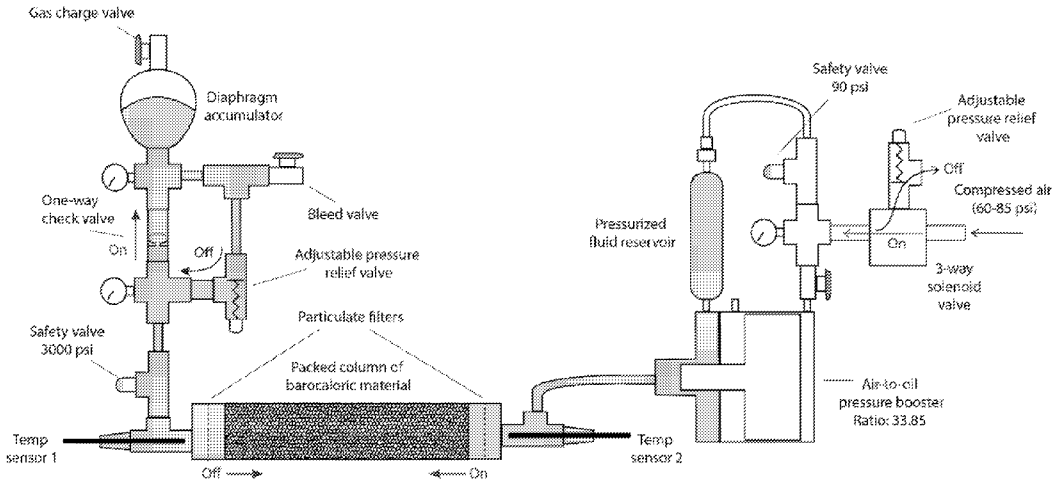
(54) Title: DEVICE, METHODS, AND SYSTEMS FOR REGENERATIVE BAROCALORIC HEAT TRANSFER

Fig. 3



(57) Abstract: The invention provides devices, methods, and systems for barocaloric heat transfer.

[Continued on next page]

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DEVICE, METHODS, AND SYSTEMS FOR REGENERATIVE BAROCALORIC HEAT TRANSFER

BACKGROUND OF THE INVENTION

Traditional vapor-compression cooling (or heating, e.g., in a heat pump) utilizes potent greenhouse gases, the accidental release of which currently accounts for more than 4% of all planetary warming. Efficient alternative cooling technologies based on solid-state materials have the potential to displace vapor-compression, eliminating this source of emissions.

Thus, there is a need for devices for barocaloric regenerative applications.

SUMMARY OF THE INVENTION

The invention provides devices, systems, and methods for regenerative heat transfer, e.g., cooling systems, heat pumps, etc., using barocaloric materials.

In an aspect, the invention provides a device for regenerative heat transfer. The device includes a first chamber including a barocaloric material, a working fluid in thermal contact with the barocaloric material, a second chamber in fluid communication with the first chamber and a third chamber in fluid communication with the first chamber. The first chamber is fluidically disposed between the second and third chambers such that providing mechanical energy to the working fluid in the second chamber forces the working fluid through the first chamber into the third chamber. The third chamber is configured to store mechanical energy transmitted from the second chamber, and the device is configured to release the stored working fluid back into the first and second chambers.

In embodiments, the device includes a first channel fluidically disposed between the first and third chambers and configured to prevent backflow of fluid from the third chamber to the first chamber. In embodiments, the device further includes a check valve in the first channel. In embodiments, the device further includes a second channel fluidically disposed between the first and third chambers and includes a control valve configured to allow flow of the working fluid from the third chamber to the first chamber.

In embodiments, the third chamber is, or is in fluid communication with, an accumulator. The accumulator may be a hydraulic accumulator, a spring, a piston, an elastic bladder, a raised weight, a diaphragm accumulator, or a pneumatic or hydraulic cylinder.

In embodiments, the third chamber is configured to store the working fluid at a pressure provided to the working fluid by the mechanical energy provided in the second chamber. In embodiments, the working fluid is a gas or a liquid, or a combination thereof (e.g., a gas dissolved in a liquid).

In embodiments, barocaloric material includes a 2D hybrid perovskite, a 3D hybrid perovskite, a di-n-hydrocarbyl (e.g., alkyl) ammonium salt, an intercalation compound, a layered metallo- hydrocarbyl (e.g., alkyl) phosphonate, an organic plastic crystal, a natural rubber, a synthetic rubber, an intermetallic compound, a smectite, a shape-memory alloy, an antiferromagnetic compound, an ionic-conducting salt, a ferroelectric ceramic, a ferrielectric organic salt, hydrocarbyl (e.g., alkyl) -modified layered silicates, hydrocarbyl (e.g., alkyl) ammonium-modified layered silicates, a long-chain n-alkane, layered silver

thiolates, a spin-crossover compound (e.g., $[Fe(R\text{-}Trz)_3][A]_2$, where R-Trz is a triazole ligand and A is an anion or combination of anions), an organic molecule-based switchable dielectric, a phase-change material, or a combination thereof.

In certain embodiments, the barocaloric material includes a 2D hybrid perovskite and/or a n- hydrocarbyl (e.g., alkyl) or di-n- hydrocarbyl (e.g., alkyl) ammonium salt. In some embodiments, the barocaloric material is a conventional barocaloric material. In embodiments, the barocaloric material is an inverse barocaloric material. In embodiments, the barocaloric material is a foam, a powder, pellets, a surface coating, beads, a frit, crystals, a porous gel, a packed column, or a combination thereof. In some embodiments, the barocaloric material is a multicaloric material (e.g., have both barocaloric properties and electro- and/or magnetocaloric properties). In some embodiments, the barocaloric material is not a magnetocaloric or electrocaloric material.

In embodiments, the device further includes one or more additional first chambers fluidically disposed between the second and third chambers, e.g., where each first chamber includes a different barocaloric material. In embodiments, oscillation of the working fluid between the second and third chambers induces a temperature difference between the second and third chambers.

In embodiments, the device further includes one or more heat exchangers in thermal contact with the working fluid in the second and/or third chamber.

In embodiments, the device further includes one or more temperature sensors, one or more pressure sensors, one or more fluid detectors, one or more flowmeters, one or more pressure release valves, one or more flow control valves, one or more bleed valves, one or more filters, or a combination thereof.

In some embodiments, the third chamber is in fluid communication with a source of mechanical energy. In some embodiments, both the third and second chambers are in fluid communication with a source of mechanical energy. In some embodiments, a control valve (e.g., a directional control valve or a three-way solenoid valve) fluidically disposed between the source of mechanical energy and the second and third chambers is configured to allow pumping of the working fluid from the second chamber to the third chamber and from the third chamber to the second chamber alternately, e.g., with pressure control accomplished by a separate system of relief valves.

In another aspect, the invention provides a method of exchanging heat. The method includes providing a device of the invention, pumping the working fluid from the second chamber to the third chamber thereby pressurizing the working fluid and inducing a phase change in the barocaloric material, and releasing the working fluid from the third chamber back to the second chamber thereby depressurizing the working fluid and reversing the phase change in the barocaloric material.

In some embodiments, the method includes a pressure swing of up to 400 bar (e.g., from 1 bar to 400 bar).

In another aspect, the invention provides a system for regenerative heat transfer. The system includes a device of the invention, and at least one of: i) a source of mechanical energy, ii) one or more heat sinks, iii) a power source, and iv) a computer.

Definitions

The term "about," as used herein, refers to ±10% of a recited value.

By "hydrocarbyl" is meant straight chain or branched saturated or unsaturated groups of carbons. Exemplary hydrocarbyl groups include alkyl (saturated), alkenyl (unsaturated with at least one carbon double bond and no carbon triple bonds), and alkynyl (unsaturated with at least one carbon triple bond). Alkyl groups are exemplified by n-, sec-, iso-, and tert-butyl, neopentyl, nonyl, decyl, and the like, and may be optionally substituted with one or more substituents. Hydrocarbyl groups of the invention may include 1 or more carbon atoms, e.g., greater than 2, e.g., 6-15, such as 8-12, or 4-36 in the main chain. Carbon atoms in the main chain may or may not be interrupted with one or more heteroatoms, e.g., O, S, or N.

By "aryl" is meant an aromatic cyclic group in which the ring atoms are all carbon. Exemplary aryl groups include phenyl, naphthyl, and anthracenyl. Aryl groups may be optionally substituted with one or more substituents.

By "carbocyclyl" is meant a non-aromatic cyclic group in which the ring atoms are all carbon. Exemplary carbocyclyl groups include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl. Carbocyclyl groups may be optionally substituted with one or more substituents. A carbocyclyl group may or may not be saturated.

By "fluidically disposed between" is meant a relationship between subject and object device elements in which the subject element(s) is/are in a flow path between the object elements. For example, fluid can flow from the second chamber to the third chamber via the first chamber. The term does not proscribe other flow paths between the same object elements.

By "halo" is meant, fluoro, chloro, bromo, or iodo.

By "heteroaryl" is meant an aromatic cyclic group in which the ring atoms include at least one carbon and at least one O, N, or S atom, provided that at least three ring atoms are present. Exemplary heteroaryl groups include oxazolyl, isoxazolyl, tetrazolyl, pyridyl, thienyl, furyl, pyrrolyl, imidazolyl, pyrimidinyl, thiazolyl, indolyl, quinolinyl, isoquinolinyl, benzofuryl, benzothienyl, pyrazolyl, pyrazinyl, pyridazinyl, isothiazolyl, benzimidazolyl, benzothiazolyl, benzoxazolyl, oxadiazolyl, thiadiazolyl, and triazolyl. Heteroaryl groups may be optionally substituted with one or more substituents.

By "heterocyclyl" is meant a non-aromatic cyclic group in which the ring atoms include at least one carbon and at least one O, N, or S atom, provided that at least three ring atoms are present. Exemplary heterocyclyl groups include epoxide, thiiranyl, aziridinyl, azetidinyl, thietanyl, dioxetanyl, morpholinyl, thiomorpholinyl, piperazinyl, piperidinyl, pyrrolidinyl, tetrahydropyranyl, tetrahydrofuranyl, dihydrofuranyl, tetrahydrothienyl, dihydrothienyl, dihydroindolyl, tetrahydroquinolyl, tetrahydroisoquinolyl, pyranyl, pyrazolinyl, pyrazolidinyl, dihydropyranyl, tetrahydroquinolyl, imidazolinyl, imidazolidinyl, pyrrolinyl,

oxazolidinyl, isoxazolidinyl, thiazolidinyl, isothiazolidinyl, dithiazolyl, and 1,3-dioxanyl. Heterocyclyl groups may be optionally substituted with one or more substituents.

By "in fluid communication with" is meant a connection between at least two device elements, e.g., first and second chambers, etc., that allows for fluid to move between such device elements with or without passing through one or more intervening device elements.

Optional substituents include halo, optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$; $-N(R_a)_2$; $-C(=O)R_a$; $-C(=O)OR_a$; $-S(=O)_2R_a$; $-S(=O)_2OR_a$; $-P(=O)R_{a2}$; -O-$P(=O)(OR_a)_2$, or $-P(=O)(OR_a)_2$, or an ion thereof; wherein each R_a is independently H, optionally substituted C_{1-36} hydrocarbyl (e.g., C_{1-36} alkyl); optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; or optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S. Cyclic groups may also be substituted with C_{1-36} hydrocarbyl (e.g., C_{1-36} alkyl).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a representation of a barocaloric cooling cycle. Pressurization of a barocaloric material induces a phase transition that releases heat. This heat can be transferred to a heat sink. The pressure is then released, reversing the phase transition, and absorbing heat, e.g., from a heat source.

Fig. 2 is a representation of a passive thermal regenerator, acting as a heat exchanger.

Fig. 3 shows a schematic of an active barocaloric regenerator device of the invention. The barocaloric material was placed in a central column. When the fluid in the device was pressurized by the booster on the right, fluid flowed through the column from right to left and entered the diaphragm accumulator at top left. When the pressure was released, the accumulator ejected its internal fluid driving flow from left to right. Over many cycles, one temperature sensor detected a temperature increase, and one temperature sensor detected a temperature decrease.

DETAILED DESCRIPTION OF THE INVENTION

The invention provides high-pressure devices designed to produce a heat transfer (e.g., cooling or heating) effect when paired with a suitable barocaloric material, systems including such devices, and methods of their use.

Barocaloric materials undergo solid-solid phase transitions with large latent heats and high sensitivity to pressure. This pressure-sensitivity enables the phase transition to be triggered by the application of pressure, allowing the material to perform a thermodynamic cooling cycle (see, e.g., Fig. 1). However, no practical device demonstrating a cooling effect with barocaloric materials has been produced until now. Real cooling from a barocaloric material may involve:

(1) Generate sufficient pressure to trigger the barocaloric phase transition.

(2) Transmit that generated pressure to the barocaloric material.

(3) Absorb heat from and inject heat into the barocaloric material at different points in the thermodynamic cycle.

(4) Ensure the source of the injected heat and the sink where the absorbed heat is deposited are thermally (e.g., spatially, by insulation, etc.) separated, resulting in a cooling of the heat source and a heating of the heat sink.

Devices

Compared to standard regenerative heat exchangers, the invention differs in several ways. First, barocaloric materials are incorporated into the central chamber enabling active heat transfer (e.g., cooling). Second, the device operates with larger pressure swings (for example, from 1 – 400 bar) than a regenerator which is typically at near-constant pressure. Third, the device may incorporate a unique method of concurrently reversing the direction of fluid flow and releasing the pressure, utilizing a hydraulic accumulator and a system of one-way valves. When the system is pressurized by applying mechanical energy (e.g., from a pressure source) to the working fluid in the second chamber, the third chamber admits fluid into its housing storing mechanical (e.g., hydraulic energy), e.g., with an accumulator (e.g., a spring, piston, compressed gas bladder, raised weight, or other accumulator). Working fluid is allowed to return to the second chamber (e.g., by releasing external pressure and/or opening a control valve disposed between the third and first chamber), and the stored mechanical energy (e.g., via the accumulator) is released, so that the pressure drops concurrently with the return of the working fluid. In some devices, the stored mechanical energy itself pushes the internalized fluid of the third chamber back through the device, reversing the direction of flow, while concurrently the pressure is decreased. In some devices, a second source of mechanical energy (e.g., a compressor) is used to pump the working fluid back into the second chamber while a system of pressure release valves releases the stored mechanical energy (i.e., lowers the pressure).

A device of the invention is shown in Fig. 3. A device may include three chambers: A first chamber including the barocaloric material, e.g., in a column sandwiched between two filters (e.g., frits), a second chamber in fluid communication with the first chamber and which includes or can be coupled to a source of mechanical energy (e.g., an air compressor, an air-to-oil booster, a hydraulic pump, a piston-driven by an electric motor or combustion engine, etc.), and a third chamber in fluid communication with the first chamber and including or coupled to a feature that stores mechanical energy (e.g., an accumulator, e.g., a diaphragm accumulator). The first chamber includes a working fluid (e.g., air, water, hydraulic oil, etc.) in contact with the barocaloric material (e.g., a 2D hybrid perovskite), and is fluidically disposed between the second and third chambers, such that working fluid pumped from the second chamber is in thermal contact with the barocaloric material on its way into the third chamber. The third chamber may be a pressure-tolerant vessel that stores the mechanical energy by containing the fluid pressurized by the source of mechanical energy. Alternatively, the chamber may include a component that is compressed by the working fluid (e.g., a spring or a piston, or a gas behind a diaphragm), expanded (e.g., an elastic bladder), or otherwise moved against a force, such as a weight that is raised by the working fluid against

gravity. The third chamber may be or include a hydraulic accumulator. Alternatively, the third chamber may be in fluid communication (e.g., via piping) with the accumulator, which may be a hydraulic accumulator, a spring, a piston, an elastic bladder, a raised weight, a diaphragm accumulator, or a pneumatic cylinder, or any other suitable component for storing mechanical energy.

A thermal regenerator is a passive heat exchanger which has a central chamber that is alternately filled with hot fluid (depositing heat in the chamber) or cold fluid (absorbing heat from the chamber) in an oscillating fashion (Figure 2). In devices of the invention, this central chamber is partially filled with barocaloric material, with the remaining volume filled with one or more working fluids (e.g., a gas (e.g., an inert gas), water, or hydraulic oil, etc.). A schematic of a device of the invention is shown in Fig. 3. The working fluid acts as both a heat-transfer and pressure-transmitting medium for the barocaloric material. The design is compatible with a variety of methods to generate pressure including compressed gas, hydraulic pumps, and direct mechanical compression. Such pressure sources may be components of the device, or separate components of a system including the device.

Devices may include a first channel between the first and third chambers and configured to, e.g., containing a feature to, prevent back-flow of the working fluid from the third chamber (e.g., containing a check valve, e.g., a ball check valve, a diaphragm check valve, a swing check valve, a stop check valve, a lift-check valve, or an in-line check valve, or be configured as a Tesla valve).

Devices may release the stored working fluid and mechanical energy together in response to a stimulus, e.g., by removal of the source of mechanical energy (i.e., lowering the pressure applied to the second chamber). Alternatively, or in addition, the stored working fluid may be allowed to return (and the pressure to drop) by opening a control valve (e.g., an adjustable pressure release valve, a ball valve, a butterfly valve, a disc valve, or a gate valve), e.g., in a second channel fluidically disposed between the first and third chambers (e.g., as shown in Fig. 1). The control valve may be configured to open in response to the stimulus (e.g., mechanical actuation, an electrical signal, pilot pressure operation, etc.).

In addition to removing the pressure (e.g., in a device with no control valve), the stimulus for allowing the working fluid to return may be a stimulus applied to the control valve, as stimulus such as mechanical actuation, a particular fluid pressure, an electrical signal, temperature, a fluid level, or a combination thereof.

The device may include more than one first chamber between the second and third chambers, e.g., a series of chambers, e.g., where each first chamber includes a different barocaloric material. Such a device may increase the temperature differential between the second and third chambers that the barocaloric effect produces by using barocaloric materials with different transition temperatures or pressures.

In some devices, the third chamber may be in fluid communication with a source of mechanical energy (e.g., a compressor), for example, when both the third and second chambers are in fluid communication with the same source of mechanical energy (e.g., the same compressor). In such embodiments, a control

valve (e.g., a directional control valve or a three-way solenoid valve) may be fluidically disposed between the source of mechanical energy and the second and third chambers to switch the connection to the source of mechanical energy from the second chamber to the third chamber to alternately pump the working fluid between the second and third chambers. Pressure control in devices utilizing active pumping of working fluid from the third chamber may be achieved with a separate system of relief valves, e.g., to allow the pumping from the third chamber to the second chamber to proceed at a lower pressure. Alternatively, both the third and second chambers may each be in fluid communication with separate sources of mechanical energy (e.g., each connected to its own compressor).

Devices may include heat exchangers (e.g., heat sinks, or heat transfer components, e.g., high surface area, high conductivity components, e.g., a metal honeycomb or fin structure). Such components need to be in thermal contact with the working fluid. Thermal contact may be direct physical contact or transmitted through a wall of the second or third chambers (e.g., where the chambers are made of a high heat conductivity material, e.g., a metal, e.g., steel (e.g., stainless steel), brass, copper, bronze, etc.).

Devices of the invention may also include temperature sensors (e.g., to determine when to apply or remove pressure from the working fluid, e.g., at a determined level of warming or cooling), pressure sensors (e.g., to monitor the device, and/or to determined when to restart a cycle), fluid detectors, flowmeters, pressure release valves (e.g., for safety, e.g., burst valves.), control valves (e.g., adjustable or switchable control valves, e.g., solenoid valves), needle valves, or bleed valves.

Barocaloric Materials

Any barocaloric material, i.e., any material that undergoes a solid-phase transition that is endergonic or exergonic in response to a pressure change may serve as the barocaloric material in devices of the invention.

Suitable barocaloric material includes 2D hybrid perovskites (e.g., including layers of confined organic chains between layers of inorganic salts), 3D hybrid perovskites, intercalation compounds (e.g., transition metal intercalation compounds), smectites (e.g., montmorillonite having organic compounds intercalated therein), layered metallo- hydrocarbyl (e.g., alkyl) phosphonate, an organic plastic crystal, a natural rubber, a synthetic rubber, an intermetallic compound, a shape-memory alloy, an antiferromagnetic compound, an ionic-conducting salt, di-n- hydrocarbyl (e.g., alkyl) ammonium salts, ferroelectric ceramics, ferrielectric organic salts, hydrocarbyl (e.g., alkyl) -modified layered silicates, hydrocarbyl (e.g., alkyl) ammonium-modified layered silicates, long-chain n-alkanes, layered silver thiolates, organic molecule-based switchable dielectrics, a spin-crossover compound, a phase-change material, or combinations thereof. The barocaloric material may be a multicaloric material. The barocaloric material may also be magnetocaloric, photocaloric, electrocaloric, etc. The barocaloric material may be a material that is not a magnetocaloric or electrocaloric material.

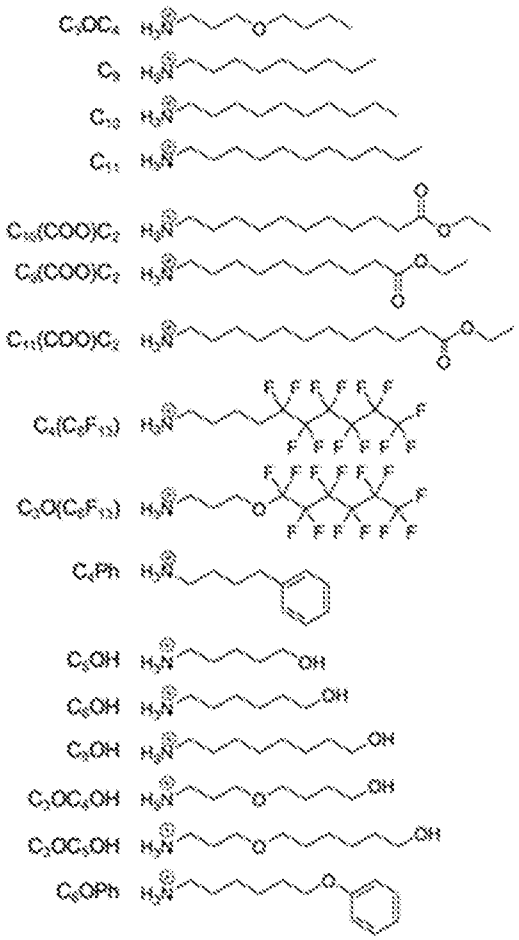
In some embodiments, the barocaloric material is a conventional barocaloric material. In embodiments, the barocaloric material is an inverse barocaloric material (i.e., where the increase in pressure leads to a decrease in transition temperature (i.e., $dT/dP < 0$)). When an inverse barocaloric material is used, the

cycle may be reversed, or the placement of heat exchangers may be switched vs. a conventional barocaloric material. The barocaloric material may be in any suitable form, for example, a foam (e.g., an open-celled foam), a powder (e.g., a fluidized powder), pellets, a surface coating (e.g., on one of the other forms described herein), beads (e.g., beads of the barocaloric material, or multilayered beads having the barocaloric material as a component, e.g., as a coating), a frit (e.g., sintered pellets, beads, particles, powder, etc., having high porosity, or e.g., a frit of another sintered material, such as ceramic or metal, having a coating of the barocaloric material), crystals, a porous gel, a packed column, etc. Barocaloric materials of the invention may be shaped using one or more additives, e.g., binders, thermally conductive additives (e.g., graphite flakes), etc. Barocaloric materials are preferentially provided in a physical form that affords high surface area while allowing for fluid flow. Barocaloric materials may also be preferentially provided in a form that confers high thermal conductivity.

Exemplary barocaloric materials may be layered materials having an organic layer including optionally substituted $C_{>3}$ hydrocarbyl (e.g., alkyl) chains (e.g., $C_{>4}$ hydrocarbyl (e.g., alkyl) chains), between first and second inorganic layers or includes a head group capable of hydrogen bonding, halogen bonding, and/or electrostatic interaction with a counterion (e.g., an anion such as a halide). The organic layer having a disordered state and an ordered state, which pressure causes transitions between.

The organic layers may include two different molecular structures. In some embodiments, the first and second inorganic layers include a silicate. In some embodiments, the barocaloric material may include a metal hydrocarbyl (e.g., alkyl) phosphonate salt. In certain embodiments, the barocaloric material includes a 2D hybrid perovskite and/or a n- hydrocarbyl (e.g., alkyl) or di-n- hydrocarbyl (e.g., alkyl) ammonium salt.

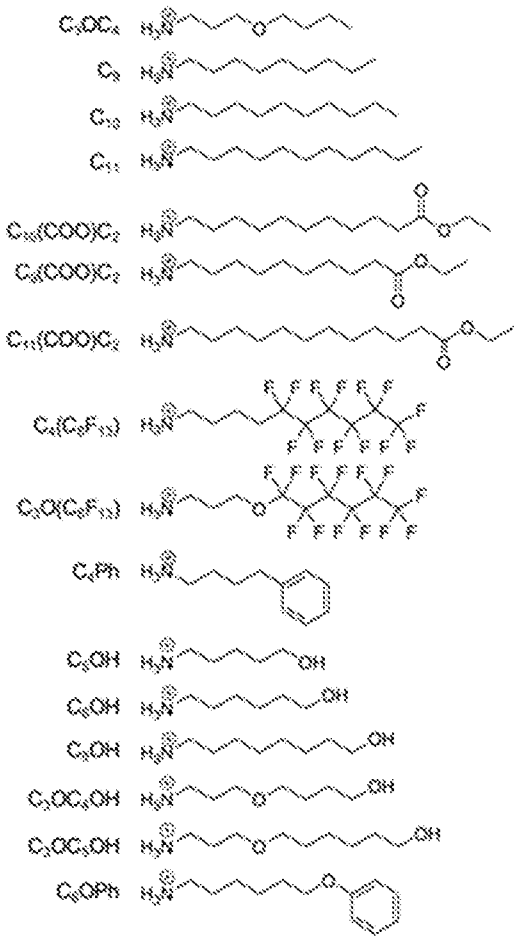
A 2D hybrid perovskite may include first and second layers of a transition metal halide and an organic layer. For example, an organic layer including a $C_{>3}$ hydrocarbyl (e.g., alkyl) (e.g., $C_{>4}$ hydrocarbyl (e.g., alkyl), e.g., $C_{4\text{-}36}$ hydrocarbyl (e.g., alkyl) chains) ammonium species. For example, a hydrocarbylammonium species selected from:



2D hybrid perovskites may include a transition metal (e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Rh, Pd, Cd, Re, Pt, or Hg) halide (e.g., F, Cl, Br, or I). 2D hybrid perovskites may include an octahedral transition metal complex. In some embodiments, the transition metal halide includes a monovalent metal cation and a trivalent metal cation.

The barocaloric materials may include a 2D hybrid perovskite having formula $[(R^1)_x(R^2)_{1-x}]_2MX_yX'_{4-y}$, where R^1 and R^2 are independently optionally substituted hydrocarbyl (e.g., alkyl) ammonium species, X and X' are different halides, x is between 0-1, y is 0-4, M is a transition metal (e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Rh, Pd, Cd, Re, Pt, or Hg); and where if y = 0 or 4, $R^1 \neq R^2$ and $x \neq 0$ or 1. In some embodiments, R^1 and R^2 are independently hydrocarbylammonium species of formula $C_nH_{2n+1}NH_3^+$, where $n > 3$ (e.g., n >4, e.g., $C_{4\text{-}36}$ hydrocarbyl (e.g., $C_{4\text{-}36}$ alkyl)).

A 2D hybrid perovskite may include compounds of a formula selected from: $(NA)_2CuCl_3Br$; $(NA)_2CuCl_2Br_2$; $(NA)_2CuClBr_3$; $(DA)_2CuCl_3Br$; $(DA)_2CuCl_2Br_2$; $(DA)_2CuClBr_3$; $[(NA)_{0.75}(DA)_{0.25}]_2CuCl_4$; $[(NA)_{0.5}(DA)_{0.5}]_2CuCl_4$; $[(NA)_{0.25}(DA)_{0.75}]_2CuCl_4$; $[(NA)_{0.25}(UA)_{0.75}]_2CuCl_4$; $[(NA)_{0.5}(UA)_{0.5}]_2CuCl_4$; or $[(NA)_{0.5}(DA)_{0.5}]_2CuCl_2Br_2$. In some embodiments, R^1 and R^2 are independently hydrocarbylammonium species selected from:



. In some embodiments, X is Cl, and X' is Br.

Hydrocarbylammonium species suitable for use as organic layers in 2D hybrid perovskite barocaloric materials include compounds of formula $(C_nH_{2n+1})(C_mH_{2m+1})NH_2X$, where n is 1-3 or 4-36 and m is 4-36; and where X is a monoanionic species (e.g., a halide (e.g., F, Cl, Br, or I) or a non-halide anion, such as NO_3^-, ClO_3^-, ClO_4^-, $H_2PO_4^-$, HSO_4^-, CN^-, $HCOO^-$, N_3^-, $N(CN)_2^-$, BF_4^-, BH_4^-, PF_6^-, SCN^-, or OCN^-). In some embodiments, $n = m$ and n = 4-36. In some embodiments, n = 1-3 and m = 4-36 (e.g., where n = 1 and m = 6, 8, 10, or 12).

Suitable barocaloric materials may also include a compound of the following table:

Type	Chemical Formula
2D hybrid perovskite	$(OA)_2MnCl_4$
	$(OA)_2MnCl_4$
	$(NA)_2MnCl_4$
	$(NA)_2CuCl_4$
	$(DA)_2CuCl_4$
Mixed 2D hybrid perovskites	$(NA)_2CuCl_3Br$
	$(NA)_2CuCl_2Br_2$
	$(NA)_2CuClBr_3$
	$(DA)_2CuCl_3Br$
	$(DA)_2CuCl_2Br_2$
	$(DA)_2CuClBr_3$

	$[(NA)_{0.75}(DA)_{0.25}]_2CuCl_4$
	$[(NA)_{0.5}(DA)_{0.5}]_2CuCl_4$
	$[(NA)_{0.25}(DA)_{0.75}]_2CuCl_4$
	$[(NA)_{0.25}(UA)_{0.75}]_2CuCl_4$
	$[(NA)_{0.5}(UA)_{0.5}]_2CuCl_4$
	$[(NA)_{0.5}(DA)_{0.5}]_2CuCl_2Br_2$
Di-*n*-alkyl ammonium salt	$(n\text{-}C_6H_{13})_2NH_2Br$
	$(n\text{-}C_8H_{17})_2NH_2Cl$
	$(n\text{-}C_6H_{13})_2NH_2Cl$
	$(n\text{-}C_6H_{13})_2NH_2I$
	$(n\text{-}C_8H_{17})_2NH_2Br$
	$(n\text{-}C_{12}H_{25})_2NH_2Cl$
	$(n\text{-}C_{12}H_{25})_2NH_2Br$
	$(n\text{-}C_{10}H_{21})_2NH_2Cl$
	$(n\text{-}C_{10}H_{21})_2NH_2Br$
	$(n\text{-}C_{10}H_{21})_2NH_2I$
	$(n\text{-}C_{12}H_{25})_2NH_2Br$
	$(n\text{-}C_{18}H_{37})_2NH_2Cl$
	$(n\text{-}C_{18}H_{37})_2NH_2Br$
	$(n\text{-}C_{12}H_{25})(CH_3)NH_2Br$
	$(n\text{-}C_{12}H_{25})(CH_3)NH_2Cl$
Intercalation compound (first-row transition metal)	$FeOCl{\bullet}C_{14}H_{29}NH_2$
	$Ni(CN)_2{\bullet}C_{12}H_{25}NH_2$
	$Ni(CN)_2{\bullet}\ C_{12}H_{25}NH_2$
intercalated between montmorillonite (smectite)	$(C_{18}H_{37})_3NH^+$ *Self-Assembled Monolayer*
	$(C_{18}H_{37})_4N^+$ *Self-Assembled Monolayer*
Layered metallo–alkylphosphonate	$Mg(O_3PC_{22}H_{45})$

Where OA = octylammonium, DA = decylammonium, NA = nonylammonium, and UA = undecylammonium.

Di-n- hydrocarbyl (e.g., alkyl) ammonium salts may be suitable for use as barocaloric materials alone (i.e., not in combination with a perovskite, silicate, or metallo- hydrocarbyl (e.g., alkyl) phosphonate), for example, hydrocarbyl (e.g., alkyl) ammonium compounds having formula $(C_nH_{2n+1})(C_mH_{2m+1})NH_2X$, where n is 1-3 or 4-36 and m is 4-36; and where X is a monoanionic species (e.g., a halide (e.g., F, Cl, Br, or I) or a non-halide anion, such as NO_3^-, ClO_3^-, ClO_4^-, $H_2PO_4^-$, HSO_4^-, CN^-, $HCOO^-$, N_3^-, $N(CN)_2^-$, BF_4^-, BH_4^-, PF_6^-, SCN^-, or OCN^-). In some embodiments, $n = m$ and n = 4-36. In some embodiments, n = 1-3 and m = 4-36 (e.g., where n = 1 and m = 6, 8, 10, or 12).

Alternatively or in addition, the barocaloric material may be a spin crossover material, e.g., a material having a low spin state and a high spin state, where the low spin state has higher thermal conductivity than the high spin state, and where the material undergoes spin crossover between the low and high spin

states in response to a first stimulus (e.g., a pressure change, a temperature change, light, or any combination thereof). For example, a material including one or more first-row transition metal complexes with d^4–d^7 electron configuration in octahedral ligand field. The change in spin state induced by the stimulus may be reversed by a second stimulus, which may be of the same type of energy or a different type of energy.

Such a spin crossover material may include a transition metal coordination complex, for example, a complex of Co(ii), Co(iii) Fe(ii), Fe(iii), Ni(ii), Mn(ii), Mn(iii), Cr(ii), Pd(ii), Pt(ii), Au(i), Ag(i), Cu(ii), or a combination thereof. Spin crossover materials may include molecular transition metal complexes or 1D, 2D, or 3D polymeric transition metal complexes. 1D polymeric transition metal complexes may include bridging triazole ligands such as the 1D polymeric $[Fe(R\text{-}Trz)_3][A]_2$ (where R-Trz is a triazole ligand with an R group, e.g., an optionally substituted hydrocarbyl (e.g., alkyl) group, an optionally substituted aryl, an optionally substituted carbocyclyl group, or an optionally substituted heteroaryl group, and where A is an anion or combination of anions). An exemplary spin crossover material is bis[hydrotris(1,2,4-triazol-1-yl)borate] iron(II) ($Fe(HB(tz)_3)_2$). Other spin-crossover materials are also considered.

Working Fluids

A working fluid of the invention may be selected to have high specific heat capacity and high thermal conductivity. A working fluid may be selected such that the barocaloric material has minimal, preferably zero, solubility therein. Alternatively, the working fluid may be saturated in the barocaloric material.

The working fluid may be a gas or liquid. For example, a working fluid may be an aqueous fluid, e.g., water, or solutions or mixtures thereof. A working fluid may be a non-aqueous liquid, e.g., a molten salt, a hydrocarbon, a fluorocarbon, a silicone (e.g., low viscosity silicone), a eutectic alloy, etc. A working fluid may be a hydraulic fluid, e.g., a hydraulic oil (e.g., a hydrocarbon oil (e.g., mineral oils or synthetic hydrocarbons), fluorocarbon oils, silicone oils, etc.), a glycol ether (e.g., ethylene glycol, propylene glycol, etc.), a polyalphaolefin, an organophosphate ester, etc. A liquid working fluid may be selected to have a low compressibility, e.g., lower than 2×10^{-9} Pa at room temperature. There may be two working fluids, e.g., separated by a thermally conductive and pressure-transmitting barrier (e.g., a flexible membrane, metal sheet, etc.), e.g., such that one working fluid is oscillated between the chambers while the other remains in contact with the barocaloric material. Such an arrangement can allow, e.g., use of materials that would be otherwise incompatible with the barocaloric material, use of a working fluid that has an advantageous effect on the properties of the barocaloric material, or use of a gas and a liquid simultaneously (e.g., with the gas in physical contact with the barocaloric material and the liquid in the second and third chambers, or vice versa). Two working fluids may be immiscible, which may obviate the need for a barrier.

Examples of suitable gases include nitrogen, helium, neon, argon, krypton, xenon, methane, ethane, propane, cyclopropane, butane, ethylene, ammonia, sulfur hexafluoride, nitrous oxide, carbon dioxide, and mixtures thereof. Suitable gases may also include hydrofluorocarbon refrigerants, e.g., R134a and HFO-1234yf. Air may be a working fluid.

Other fluid states of matter are also considered, e.g., supercritical fluids. A working fluid that is a liquid or supercritical fluid may include dissolved solids, liquids, or gases, for example, as corrosion inhibitors, anti-erosion additives, anti-wear additives, etc.

In some embodiments, the gas is an inert gas that is able to permeate a free volume of the organic layer. In some embodiments, the permeated gas interacts with the barocaloric material. In some embodiments, an extent of permeation and interaction of the at least one gas with the barocaloric material together induce a lowering of a phase transition and/or a barocaloric effect inversion. In some embodiments, the change in thermal property is a lowering of a phase transition temperature and/or a barocaloric effect inversion.

Methods

Methods of the invention may include providing heat energy (e.g., from a room, an AC system, heat transfer medium, heat pump, heat sink, etc.) to a second or third chamber of a device of the invention and cycling the device through one or more regeneration cycles to transfer the heat to a heat sink in thermal contact with the corresponding third chamber (or vice versa, e.g., when using an inverse barocaloric material).

A difference in pressure between the high pressure state (e.g., the maximum pressure enforced by the mechanical energy provided) and low pressure state (e.g., at the after releasing the working fluid from the third chamber when all of the stored mechanical energy has been expended), i.e., a pressure swing, may be from 1 to 400 bar, e.g., from 1-2 bar, 1-5 bar, 1-10 bar, 1-50 bar, 1-100 bar, 1-150 bar, 1-200 bar, 1-250 bar, 5-25 bar, 25-50 bar, 25-75 bar, 100-200 bar, 100-300 bar, 150-300 bar, 200-300 bar, 250-300 bar, 100-400 bar, 150-400 bar, 200-400 bar, 250-400 bar, 300-400 bar, or 350-400 bar, e.g., from a starting pressure of 1 bar, 2 bar, 5 bar, 10 bar, 25 bar, 50 bar, 75 bar, 100 bar, 125 bar, 150 bar, 200 bar, 250 bar, 300 bar, or 350 bar, to a final pressure of 2 bar, 5 bar, 10 bar, 25 bar, 50 bar, 75 bar, 100 bar, 125 bar, 150 bar, 200 bar, 250 bar, 300 bar, 350 bar, or 300 bar, or the reverse.

In a conventional barocaloric cooling method, providing compression to the barocaloric material (by pumping working fluid from the second chamber to the third chamber) releases latent heat in the barocaloric material to the working fluid, which may be removed, e.g., via a heat sink, e.g., a high surface area, high conductivity medium in thermal contact with the working fluid and which may be itself cooled by, e.g., a fan. Removal of the heat may be performed while the barocaloric material is still compressed, and removal of the compression (by returning the working fluid to the second chamber) allows the barocaloric material to return to a disordered state, cooling the barocaloric material and working fluid as the endothermic transition occurs. At this point the cycle may be repeated with input of new heat energy, e.g., from a heat source being cooled. When the barocaloric material is an inverse barocaloric material, the cycling is the same, but the placement of the heat sink and heat source is reversed.

Methods of the invention may also include selecting or otherwise controlling the working fluid to modulate the barocaloric cycle. For example, selecting a gas (e.g., a high polarizability gas) that sufficiently permeates and interacts with the barocaloric material at the microscopic level as the working fluid to change the temperature of phase transitions in the barocaloric material, or to induce inverse barocaloric

effects such as described herein. Methods may include modulating the barocaloric cycle by altering a ratio of polarizable and non-polarizable gases in a mixture used as a working fluid. Methods may include selecting a gas as the working fluid that does not interact, or minimally interacts, with the barocaloric material (e.g., He), e.g., to not induce changes in thermal properties, or to revert changes caused by an interacting gas.

Systems and Additional Components

Systems of the invention may include components to transfer mechanical energy to the barocaloric material, e.g., pumps, pistons, actuators (e.g., mechanical, hydraulic, or pneumatic, etc., actuators), presses (e.g., mechanical, hydraulic, or pneumatic, etc., presses), piezoelectric actuators, levers, etc. Systems may also include components to transfer or remove heat energy, e.g., pumps, heat sinks, thermoelectrics, fans, chiller pumps, vortex tubes, heaters, heat tapes, etc. A system of the invention may also include a power source, e.g., to power the source of compressive force, the cooling or heat transfer components, etc. Systems of the invention may include additional pumps, reservoirs (e.g., tanks, cylinders, etc.), pressure sensors, actuators, valves, etc. Systems of the invention may include a computer (e.g., a microcontroller), e.g., for monitoring or controlling the device, e.g., to send a signal to a control valve to return the working fluid to the second chamber, to remove the pressure applied to the second chamber, and/or to open a pressure release valve to depressurize the device.

EXAMPLE

Fig. 3 shows a schematic of a device of the invention. In the device, a barocaloric material ($(NA)_2CuBr_4$) was packed in a column between two particulate filters in a pipe to make the first chamber. The second chamber (fluid reservoir) was connected to a compressed air source, an oil to air booster, and an adjustable pressure relief valve. A 3-way solenoid valve allowed for switching between "on" (compressed air into the booster) and "off" (air from booster leaves via pressure release valve) states. The third chamber (the diaphragm actuator) was connected to the opposite end of the first chamber via a channel (a series of pipes and pipe connectors including a 3000 psi safety valve and a one-way check valve). A second channel (made of pipes and pipe connectors) was connected to the first channel either side of the one-way check valve, and included another adjustable pressure release valve as a control valve between the first and third chambers. Temperature sensors connected to either side of the first chamber allowed for monitoring of the heat transfer (e.g., cooling or heating) cycle. A working fluid of low-viscosity silicone filled the volume of the device not occupied by the barocaloric material.

In the "on" (i.e., high pressure) state, the 3-way solenoid was set to direct pressure from the compressed gas source to the booster to pressurize the device (by compressing gas in the diaphragm accumulator). The second adjustable pressure relief valve remained closed because the differential pressure across the valve was below the set relief pressure. In the "off" (i.e., low pressure) state, the solenoid was switched to open the booster to the first adjustable pressure release valve, which was opened, and the decreasing pressure in the first chamber opened the second adjustable pressure release valve, allowing the working fluid to be pushed back through the barocaloric material by the diaphragm accumulator as the pressure

returned to the low pressure “off” state. Over repeated cycles, a greater difference in temperature between the temperature sensors was developed in the temperature range where the barocaloric transition was operating than at other temperature indicating successful barocaloric cooling.

Other embodiments are in the claims.

What is claimed is:

CLAIMS

1. A device for regenerative heat transfer comprising:

a) a first chamber comprising a barocaloric material;
b) a working fluid in thermal contact with the barocaloric material;
c) a second chamber in fluid communication with the first chamber; and
d) a third chamber in fluid communication with the first chamber;

wherein the first chamber is fluidically disposed between the second and third chambers; wherein providing mechanical energy to the working fluid in the second chamber forces the working fluid through the first chamber into the third chamber; wherein the third chamber is configured to store mechanical energy transmitted from the second chamber; and wherein the device is configured to release the stored working fluid back into the first and second chambers.

2. The device of claim 1, further comprising a first channel fluidically disposed between the first and third chambers and configured to prevent backflow of fluid from the third chamber to the first chamber.

3. The device of claim 2, further comprising:

e) a check valve in the first channel; and/or
f) a second channel fluidically disposed between the first and third chambers and comprising a control valve configured to allow flow of the working fluid from the third chamber to the first chamber.

4. The device of claim 1, wherein the third chamber is, or is in fluid communication with, an accumulator.

5. The device of claim 4, wherein the accumulator is a hydraulic accumulator, a spring, a piston, an elastic bladder, a raised weight, a diaphragm accumulator, or a pneumatic or hydraulic cylinder.

6. The device of claim 1, wherein the third chamber is configured to store the working fluid at a pressure provided to the working fluid by the mechanical energy provided in the second chamber.

7. The device of claim 1, wherein the working fluid is a gas or a liquid, or a combination thereof.

8. The device of claim 1, wherein barocaloric material comprises a 2D hybrid perovskite, a 3D hybrid perovskite, a di-n-hydrocarbylammonium salt, an intercalation compound, a layered metallo-hydrocarbylphosphonate, an organic plastic crystal, a natural rubber, a synthetic rubber, an intermetallic compound, a shape-memory alloy, an antiferromagnetic compound, an ionic-conducting salt, a ferroelectric ceramic, a ferrielectric organic salt, hydrocarbyl-modified layered silicates, hydrocarbylammonium-modified layered silicates, a long-chain n-alkane, layered silver thiolates, a spin-crossover compound, an organic molecule-based switchable dielectric, a phase-change material, or a combination thereof.

9. The device of claim 1, wherein the barocaloric material comprises a 2D hybrid perovskite and/or a n-hydrocarbyl or di-n-hydrocarbylammonium salt.

10. The device of claim 1, wherein the barocaloric material is a conventional barocaloric material.

11. The device of claim 1, wherein the barocaloric material is an inverse barocaloric material.

12. The device of claim 1, wherein the barocaloric material is a foam, a powder, pellets, a surface coating, beads, a frit, crystals, a porous gel, a packed column, or a combination thereof.

13. The device of claim 1, further comprising one or more additional first chambers fluidically disposed between the second and third chambers, wherein each first chamber comprises a different barocaloric material.

14. The device of claim 1, wherein oscillation of the working fluid between the second and third chambers induces a temperature difference between the second and third chambers.

15. The device of claim 1, further comprising one or more heat exchangers in thermal contact with the working fluid in the second and/or third chamber.

16. The device of claim 1, wherein the barocaloric material is a multicaloric material.

17. The device of claim 1, wherein the barocaloric material is not a magnetocaloric or electrocaloric material.

18. The device of claim 1, further comprising one or more temperature sensors, one or more pressure sensors, one or more fluid detectors, one or more flowmeters, one or more pressure release valves, one or more flow control valves, one or more bleed valves, one or more filters, or a combination thereof.

19. The device of claim 1, wherein the third chamber is in fluid communication with a source of mechanical energy.

20. The device of claim 1, wherein both the third and second chambers are in fluid communication with a source of mechanical energy.

21. The device of claim 20, further comprising a control valve fluidically disposed between the source of mechanical energy and the second and third chambers, wherein the control valve is configured to alternately allow pumping of the working fluid from the second chamber to the third chamber and from the third chamber to the second chamber.

22. A method of exchanging heat comprising:

a) providing the device of claim 1;
b) pumping the working fluid from the second chamber to the third chamber thereby pressurizing the working fluid and inducing a phase change in the barocaloric material; and
c) releasing the working fluid from the third chamber back to the second chamber thereby depressurizing the working fluid and reversing the phase change in the barocaloric material.

23. The method of claim 22, comprising a pressure swing of up to 400 bar.

24. A system for regenerative heat transfer comprising:

a) the device of claim 1; and
b) at least one of:
    i) a source of mechanical energy,
    ii) one or more heat sinks,
    iii) a power source, and
    iv) a computer.

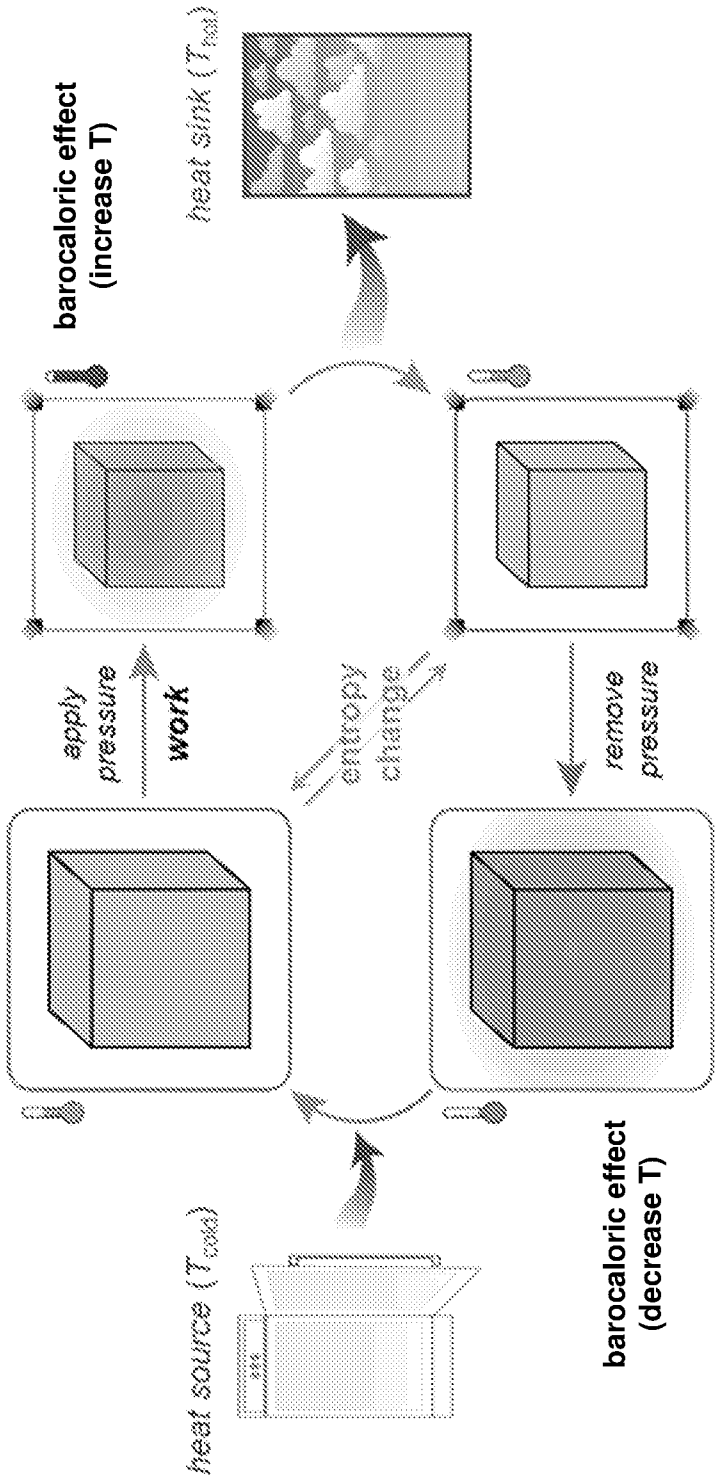

barocaloric effect
(increase T)
heat sink (T_{hot})
apply
pressure
work
entropy
change
remove
pressure
heat source (T_{cold})
barocaloric effect
(decrease T)

Fig. 1

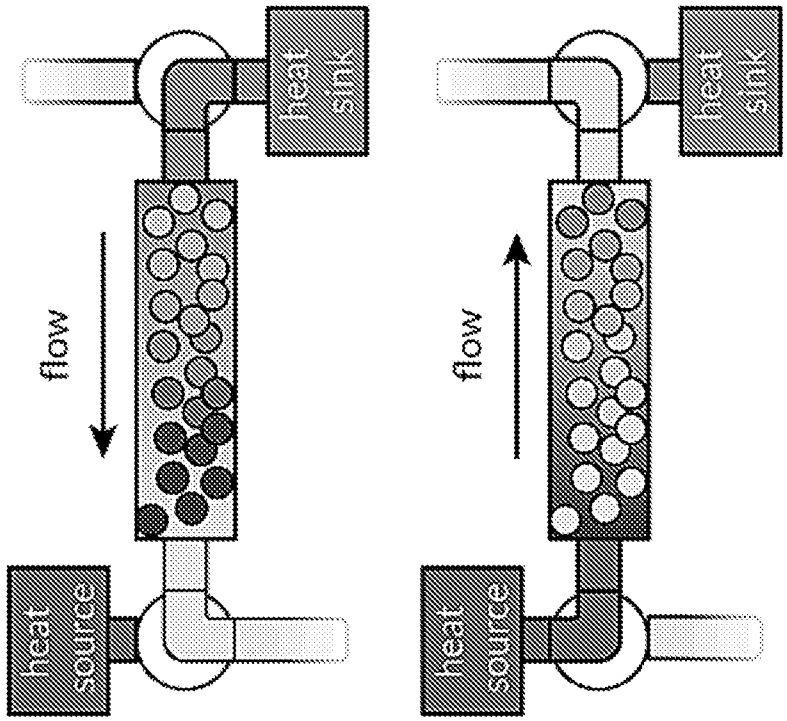
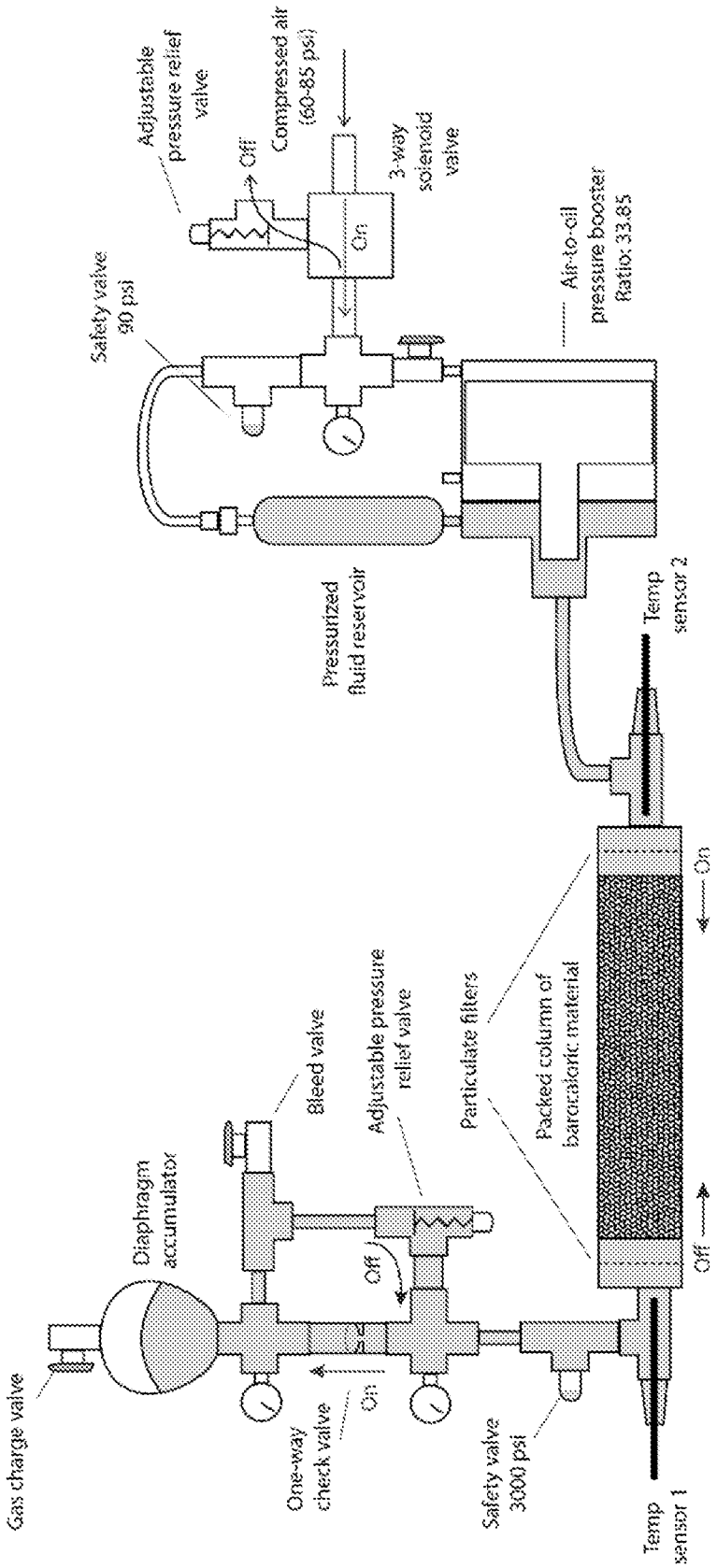


Fig. 2

Fig. 3


Gas charge valve
Diaphragm accumulator
Bleed valve
Adjustable pressure relief valve
Off
On
One-way check valve
Particulate filters
Packed column of barocaloric material
On
Off
Safety valve 3000 psi
Temp sensor 1
Temp sensor 2
Pressurized fluid reservoir
Safety valve 90 psi
Adjustable pressure relief valve
Off
Compressed air (60-85 psi)
3-way solenoid valve
On
Air-to-oil pressure booster Ratio: 33.85

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 23/30349

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. F03G 7/06, F28D 17/04 (2023.01),
ADD. F28F 23/00, F25B 23/00, F25B 30/00 (2023.01)

CPC - INV. F03G 7/0646, F03G 7/064, F03G 7/063, F03G 7/0614, F03G 7/061, F03G 7/06, F03G 7/062, F28D 17/04

ADD. F28F 23/00, F28F 13/003, F25B 23/00, F25B 30/00

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)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2019/0032969 A1 (Fraunhofer - Gesellschaft zur Forderung der Angewandten Forschung E.V), 31 January 2019 (31.01.2019), entire document, especially Figs 1-6	1-24
A	US 2021/0341232 A1 (GORENJE GOSPODINJSKI APARATI , D.D), 04 November 2021 (04.11.2021), entire document, especially Figs 1-29	1-24
A	US 2020/0378655 A1 (Haier US Appliance Solutions, Inc), 03 December 2020 (03.12.2020), entire document, especially Figs 1-5	1-24
A	US 2018/0371959 A1 (Thermolectric Industrial Solutions GmbH), 27 December 2018 (27.12.2018), entire document	1-24
A	US 2012/0192979 A1 (Barth et al), 02 August 2012 (02.08.2012), entire document	1-24

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
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"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
13 October 2023	NOV 06 2023
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300