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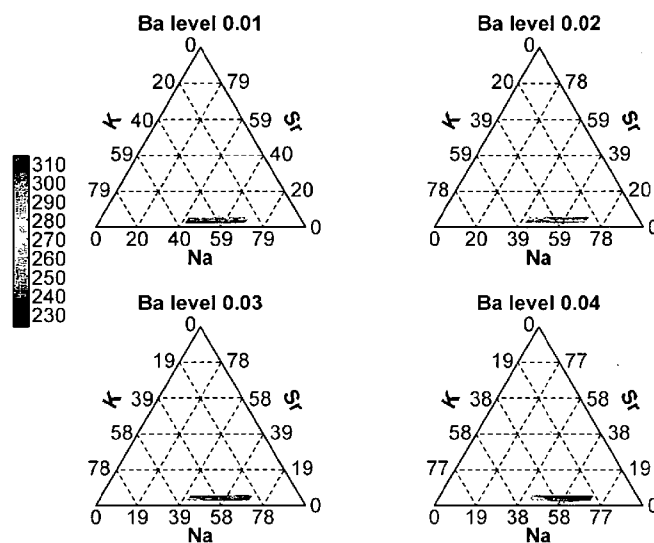


FIG. 1

(57) Abstract: Several systems of low-cost, thermally stable inorganic salts are disclosed. These compositions include earth-abundant salt materials and can have thermal stability limits greater than 600°C.

MOLTEN SALT MATERIAL FOR HEAT TRANSFER AND THERMAL ENERGY STORAGE

CROSS-REFERENCES TO RELATED APPLICATIONS

- 5 **[0001]** This application claims priority to U.S. Provisional Application No. 61/485,491, filed May 12, 2011, which is incorporated in its entirety herein for all purposes.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

- 10 **[0002]** This invention was made with Government support under Grant No. DE-FG36-08GO18144 awarded by Department of Energy. The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

- 15 **[0003]** It is imperative that we reduce our usage of natural gas and especially coal to address pressing societal concerns such as climate change and environmental degradation, energy security, and price volatility. Solar thermal power, a compelling source of renewable electricity at large scale, represents a possible solution to fossil fuel use. With further technological advances, solar thermal power will become cheaper than natural gas or coal and
20 able to provide electricity day and night. However, electricity from solar thermal power currently costs approximately \$0.15 per kilowatt hour. This cost is too high to be directly competitive with fossil fuel-based power, which can cost \$0.10 per kilowatt hour or less.

- 25 **[0004]** The solar thermal power market is an emerging industry with enormous growth potential. A recent report published by Greenpeace and the European Solar Thermal Electricity Association projects an installed capacity over 68,000 MW by 2020, enough to power over 50 million households ["Concentrating solar power outlook 2009," Greenpeace International, SolarPACES, and ESTELA, 2009]. Solar thermal power plants generate electricity by focusing sunlight using mirrors onto a receiver, then passing a fluid through the receiver to collect the heat, and finally using the heated fluid to boil water and drive a steam turbine generator. At the heart
30 of these plants is the heat transfer fluid. The market for this crucial component is projected to reach \$5.5 billion by 2020. It is possible to store large quantities of the heated fluid in an

insulated tank during the day, and to discharge this thermal energy after sundown to continue generating power ["Survey of thermal storage for parabolic trough power plants," subcontractor report NREL/SR-550-27925, 2000]. However, this storage represents an additional capital cost to the project developer and must be made cheaper in order to economically provide power from the sun day and night.

[0005] In order to achieve large scale commercial deployment and to compete with fossil fuels, there is a crucial need across the solar thermal power industry to lower costs and develop viable thermal storage. To achieve these goals solar technology developers are pushing to increase the operating temperature of their systems, thereby lowering their levelized cost of the electricity and reducing the cost of storage. The need for high temperatures has led to the adoption of molten salt heat transfer fluids (HTFs) and thermal storage materials as opposed to synthetic oils, which can break down, and steam, which generates excessively high pressure. Users need an advanced, low cost molten salt to achieve their goals.

[0006] A molten salt with a broad operating range (low melting point, high thermal stability) would be a transformative technology for applications in addition to solar thermal power. Such a material would enable in-situ oil shale conversion, in which solar thermal energy is used to heat oil shale underground and convert it at high temperature into an upgraded liquid product that can be extracted by conventional means ["In situ conversion process fact sheet," Royal Dutch Shell, May 2008]. Additional applications include heat transfer and heat storage with industrial processes, heat treating of metals, and as an electrolyte in thermal batteries [P. Masset and R. Guidotti, "Thermal activated (thermal) battery technology Part II. Molten salt electrolytes," J. Power Sources, vol. 164, pp. 397-414, 2007].

[0007] The current standard HTF salt considered for central receiver applications, called "solar salt," is a mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate. Solar salt has a melting point of approximately 240°C and a maximum temperature of 565 °C ["Hitec solar salt," Coastal Chemical Co., LLC]. It is subject to significant price volatility due to supply constraints and other applications of its components, such as for fertilizer.

Accordingly, there exists a need for an affordable molten salt heat transfer fluid that is composed of low-cost materials and exhibits a broad operating temperature range. Surprisingly, the present invention addresses this and other needs.

BRIEF SUMMARY OF THE INVENTION

[0008] In some embodiments, the present invention provides a composition including a sodium cation, in an amount of from about 55 to about 85 mol % based on the cations; a potassium cation, in an amount of from about 15 to about 40 mol % based on the cations; and
5 a nitrate anion, in an amount of from about 75 to about 100 mol % based on the anions. The composition also includes at least two members selected from a strontium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a barium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on the anions; and a chloride anion in an
10 amount of from about 0.1 to about 15 mol % based on the anions.

[0009] In some embodiments, the present invention provides a composition consisting essentially of a sodium cation, in an amount of from about 55 to about 85 mol % based on the cations; a potassium cation, in an amount of from about 15 to about 40 mol % based on the cations; a nitrate anion, in an amount of from about 75 to about 100 mol % based on the
15 anions; and at least two members selected from a strontium cation, in an amount of from about 0.1 to about 10 mol % based on the cations, a barium cation, in an amount of from about 0.1 to about 10 mol % based on the cations, a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on the anions, and a chloride anion in an amount of from about 0.1 to about 15 mol % based on the anions.

20 [0010] In some embodiments, the present invention provides a method for storing solar thermal energy. The method includes exposing a composition to sunlight, wherein the composition contains a sodium cation, in an amount of from about 55 to about 85 mol % based on the cations; a potassium cation, in an amount of from about 15 to about 40 mol % based on the cations; and a nitrate anion, in an amount of from about 75 to about 100 mol %
25 based on the anions. The composition also contains at least one member selected from a strontium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a barium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on the anions; and a chloride anion in an amount of from about 0.1 to about 15 mol % based on the anions.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0011] **Figure 1** shows phase diagrams with melting point data for strontium-barium Examples 1-3 and other inventive salt mixtures in the same compositional range.

[0012] **Figure 2** shows thermal stability data for Example 1 in air as assessed by thermogravimetric analysis.

[0013] **Figure 3** shows thermal stability data for Example 1 in nitrogen as assessed by thermogravimetric analysis.

5 [0014] **Figure 4** shows phase diagrams with melting point data for sulfate-chloride Examples 24-27 and other inventive salt mixtures in the same compositional range.

[0015] **Figure 5** shows expanded phase diagrams with melting point data for sulfate-chloride Examples 24-27 and other inventive salt mixtures in the same compositional range.

10 [0016] **Figure 6** shows phase diagrams with melting point data for strontium-chloride Examples 15-17 and other inventive salt mixtures in the same compositional range.

[0017] **Figure 7** shows phase diagrams with melting point data for barium-chloride Examples 18-20 and other inventive salt mixtures in the same compositional range.

DETAILED DESCRIPTION OF THE INVENTION

15 I. General

[0018] The present invention addresses the need for a high stability, low cost molten material for salt heat transfer and thermal energy storage. The present invention is based on the surprising discovery that earth-abundant salt materials can be added to solar salt mixtures and maintain desirable physical properties (such as a broad operating range), while reducing
20 the cost of the compositions. The resulting compositions can reduce the cost of solar thermal power and enable economical thermal storage.

II. Definitions

[0019] "Cation" refers to chemical elements or counterions having a positive charge. The positive charge can be +1, +2, +3, or greater. Exemplary cations of the present invention
25 include, but are not limited to, Na^+ , K^+ , Sr^{2+} , and Ba^{2+} . Other cations are useful in the present invention.

[0020] "Anion" refers to chemical elements and counterions having a negative charge. The negative charge can be -1, -2, -3, or greater. Exemplary anions of the present invention include nitrate (NO_3^-), sulfate (SO_4^{2-}) and Cl^- . Other anions are useful in the present
30 invention.

III. Compositions

[0021] Molten salts exhibit many desirable heat transfer qualities at high temperatures. They have high density, high heat capacity, high thermal stability, and very low vapor pressure even at elevated temperatures. Their viscosity is low enough for sufficient pumping
5 at high temperatures, and many are compatible with common stainless steels. The low-cost, thermally stable compositions of the present invention were discovered by formulating and evaluating over 5000 unique salt mixtures using combinatorial chemistry techniques.

[0022] Accordingly, the present invention provides a composition including a sodium cation, a potassium cation, and a nitrate anion. The composition also includes at least one
10 member selected from a strontium cation, a barium cation, a sulfate anion, and a chloride anion. As used herein, the terms "sodium," "potassium," "strontium," and "barium" refer to the corresponding ions unless otherwise specified. In some embodiments, the present invention provides a composition including: a sodium cation, in an amount of from about 55 to about 85 mol % based on the cations; a potassium cation, in an amount of from about 15 to
15 about 40 mol % based on the cations; a nitrate anion, in an amount of from about 75 to about 100 mol % based on the anions. The composition also includes at least one member selected from the group consisting of a strontium cation, in an amount of from about 0.1 to about 10 mol % based on the cations, a barium cation, in an amount of from about 0.1 to about 10 mol % based on the cations, a sulfate anion, in an amount of from about 0.1 to about 15 mol %
20 based on the anions, and a chloride anion in an amount of from about 0.1 to about 15 mol % based on the anions.

[0023] Any suitable amount of sodium can be used in the compositions of the invention. In general, the compositions include from about 55 mol % to about 85 mol % sodium (based on the cations in the composition). In some embodiments, the compositions can include, for
25 example, from about 60 mol % to about 80 mol % sodium, or from about 70 mol % to about 75 mol % sodium. In other embodiments, the compositions can include about 55, 60, 65, 70, 75, 80, or 85 mol % sodium. In some other embodiments, the compositions can include about 73, 73.5, 74, 74.5, 75, 75.5, or 76 mol % sodium. In some embodiments, the compositions include about 75 mol % sodium based on the cations in the composition. In
30 some embodiments, the compositions include about 75.6 mol % sodium based on the cations in the composition.

[0024] Any suitable amount of potassium can be used in the compositions of the invention. In general, the compositions include from about 15 mol % to about 40 mol % potassium

(based on the cations in the composition). In some embodiments, the compositions can include, for example, from about 20 mol % to about 35 mol % potassium, or from about 20 mol % to about 25 mol % potassium. In other embodiments, the compositions can include about 20, 25, 30, 35, or 40 mol % potassium. In some other embodiments, the compositions
5 can include about 23, 23.5, 24, 24.5, 25, 25.5, or 26 mol % potassium. In some embodiments, the compositions include about 25 mol % potassium based on the cations in the composition. In some embodiments, the compositions include about 24.4 mol % potassium based on the cations in the composition.

[0025] Any suitable amount of nitrate can be used in the compositions of the invention. In
10 general, the compositions include from about 75 mol % to about 100 mol % nitrate (based on the anions in the composition). In some embodiments, the compositions can include, for example, from about 80 mol % to about 95 mol % nitrate, or from about 85 mol % to about 90 mol % nitrate. In other embodiments, the compositions can include about 75, 80, 85, 90, 95, or 100 mol % nitrate. In some other embodiments, the compositions can include about
15 87, 87.5, 88, 88.5, 89, 89.5, 90, 90.5, 91, 91.5, or 92 mol % nitrate. In some embodiments, the compositions include about 88.3 mol % nitrate based on the anions in the composition. In some embodiments, the compositions include about 91.6 mol % nitrate based on the anions in the composition.

[0026] Any suitable amount of strontium can be used in the compositions of the invention.
20 In general, the compositions containing strontium include from about 0.1 mol % to about 10 mol % strontium (based on the cations in the composition). In some embodiments, the compositions can include, for example, from about 0.5 mol % to about 7.5 mol % strontium, or from about 1 mol % to about 5 mol % strontium. In other embodiments, the compositions can include about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 mol % strontium. In some other
25 embodiments, the compositions can be free of strontium.

[0027] Any suitable amount of barium can be used in the compositions of the invention. In general, the compositions containing barium include from about 0.1 mol % to about 10 mol % barium (based on the cations in the composition). In some embodiments, the compositions can include, for example, from about 0.5 mol % to about 7.5 mol % barium, or from about 1
30 mol % to about 5 mol % barium. In other embodiments, the compositions can include about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 mol % barium. In some other embodiments, the compositions can also be free of barium.

[0028] Any suitable amount of sulfate can be used in the compositions of the invention. In general, the compositions containing sulfate include from about 0.1 mol % to about 15 mol % sulfate (based on the anions in the composition). In some embodiments, the compositions can include, for example, from about 1 mol % to about 12 mol % sulfate, or from about 5 mol % to about 10 mol % sulfate. In other embodiments, the compositions can include about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 mol % sulfate. In some embodiments, the compositions include about 7.6 mol % sulfate based on the anions in the composition. In some embodiments, the compositions include about 4.4 mol % sulfate based on the anions in the composition. In some embodiments, the compositions include about 2.0 mol % sulfate based on the anions in the composition. In other embodiments, the compositions can be free of sulfate.

[0029] Any suitable amount of chloride can be used in the compositions of the invention. In general, the compositions containing chloride include from about 0.1 mol % to about 15 mol % chloride (based on the anions in the composition). In some embodiments, the compositions can include, for example, from about 1 mol % to about 12 mol % chloride, or from about 5 mol % to about 10 mol % chloride. In other embodiments, the compositions can include about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 mol % chloride. In some embodiments, the compositions include about 4.0 mol % chloride based on the anions in the composition. In some embodiments, the compositions include about 4.1 mol % chloride based on the anions in the composition. In some embodiments, the compositions include about 9.7 mol % chloride based on the anions in the composition. In other embodiments, the compositions can be free of chloride.

[0030] In some embodiments, the present invention provides a composition containing sodium, potassium, and nitrate, as well as two additional components selected from strontium, barium, sulfate, and chloride. The additional components can include, for example, strontium and barium, or strontium and sulfate, or strontium and chloride, or barium and sulfate, or barium and chloride, or sulfate and chloride. In some embodiments, the present invention provides a composition including a sodium cation, in an amount of from about 55 to about 85 mol % based on the cations; a potassium cation, in an amount of from about 15 to about 40 mol % based on the cations; and a nitrate anion, in an amount of from about 75 to about 100 mol % based on the anions. The composition also includes at least two members selected from a strontium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a barium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a sulfate anion, in an amount of from about 0.1 to about 15 mol % based

on the anions; and a chloride anion in an amount of from about 0.1 to about 15 mol % based on the anions.

[0031] In some embodiments, the composition includes the strontium cation and the barium cation. In some embodiments, the composition includes the sulfate anion and the chloride anion. In some embodiments, the composition includes the strontium cation and the chloride anion. In some embodiments, the composition includes the barium cation and the chloride anion. In some embodiments, the composition includes the strontium cation and the sulfate anion. In some embodiments, the composition includes the barium cation and the sulfate anion.

10 [0032] In some embodiments, the present invention provides a composition containing sodium, potassium, and nitrate, as well as three additional components selected from strontium, barium, sulfate, and chloride. The additional components can include, for example, strontium, barium, and sulfate; or strontium, barium, and chloride; or barium, sulfate, and chloride; or strontium, sulfate and chloride. In some embodiments, the present invention provides a composition including the sodium cation, the potassium cation, and the nitrate anion as described above, as well as at least three members selected from the strontium cation, the barium cation, the sulfate anion, and the chloride anion. In some embodiments, the composition includes the strontium cation, the barium cation, and the chloride anion. In some embodiments, the composition includes the strontium cation, the barium cation, and the sulfate anion. In some embodiments, the composition includes the barium cation, the sulfate anion, and the chloride anion.

[0033] In some embodiments, the composition includes the sodium cation, the potassium cation, and the nitrate anion as described above, as well as the strontium cation, the barium cation, the sulfate anion, and the chloride anion.

25 [0034] In some embodiments, the present invention provides a composition including the sodium cation in the amount of about 65 mol % based on the cations; the potassium cation in the amount of about 35 mol % based on the cations; the nitrate anion in the amount of from about 92 to about 97 mol % based on the anions; the sulfate anion in the amount of about 2 mol % based on the anions; and the chloride anion in the amount of from about 1 to about 5 mol % based on the anions.

[0035] In some embodiments, the composition includes the sodium cation in the amount of from about 64 to about 66 mol % based on the cations; the potassium cation in the amount of from about 30 to about 34 mol % based on the cations; the strontium cation in the amount of

from about 2 to about 5 mol % based on the anions; the nitrate anion in the amount of from about 94 to about 96 mol % based on the anions; and the chloride anion in the amount of from about 4 to about 6 mol % based on the anions.

[0036] In some embodiments, the composition includes the sodium cation in the amount of from about 68 to about 71 mol % based on the cations; the potassium cation in the amount of from about 25 to about 28 mol % based on the cations; the strontium cation in the amount of from about 2 to about 4 mol % based on the anions; the nitrate anion in the amount of from about 93 to about 98 mol % based on the anions; and the chloride anion in the amount of from about 2 to about 7 mol % based on the anions.

[0037] In some embodiments, the composition includes the sodium cation in the amount of from about 64 to about 66 mol % based on the cations; the potassium cation in the amount of from about 32 to about 34 mol % based on the cations; the barium cation in the amount of about 2 mol % based on the anions; the nitrate anion in the amount of from about 93 to about 97 mol % based on the anions; and the chloride anion in the amount of from about 2 to about 7 mol % based on the anions.

[0038] In some embodiments, the composition includes the sodium cation in the amount of from about 71 to about 73 mol % based on the cations; the potassium cation in the amount of from about 23 to about 25 mol % based on the cations; the barium cation in the amount of from about 2 to about 4 mol % based on the anions; the nitrate anion in the amount of from about 91 to about 93 mol % based on the anions; and the chloride anion in the amount of from about 7 to about 9 mol % based on the anions.

[0039] In some embodiments, the composition includes the sodium cation in the amount of about 69 mol % based on the cations; the potassium cation in the amount of from about 24 to about 27 mol % based on the cations; the strontium cation in the amount of from about 2 to about 4 mol % based on the anions; the barium cation in the amount of from about 1 to about 3 mol % based on the anions; the nitrate anion in the amount of from about 92 to about 94 mol % based on the anions; and the chloride anion in the amount of from about 6 to about 8 mol % based on the anions.

[0040] In some embodiments, the composition includes the sodium cation in the amount of about 64 mol % based on the cations; the potassium cation in the amount of from about 30 to about 31 mol % based on the cations; the strontium cation in the amount of from about 3 to about 5 mol % based on the anions; the barium cation in the amount of from about 1 to about

2 mol % based on the anions; and the nitrate anion in the amount of 100 mol % based on the anions.

[0041] In some embodiments, present invention provides a composition consisting essentially of any the combinations described above. That is, a composition can include the
5 ions in any of the amounts set forth above, but excludes any additional component that would alter the physical properties (*e.g.*, the melting point or the thermal stability limit) of the composition.

[0042] A composition of the present invention can be described by specifying its composition, melting point, and thermal stability. Additional properties that are relevant for
10 heat transfer fluid applications include the viscosity, specific heat, thermal conductivity, density, and vapor pressure. These properties can be measured using standard methods. The materials compatibility of the present invention with common alloys of steel is also important; this property can be measured with custom corrosion hardware.

[0043] A molten salt with a broad operating range (low melting point, high thermal
15 stability) is useful for applications in addition to concentrating solar power, such as heat transfer and heat storage with industrial processes, heat treating of metals, and as an electrolyte in thermal batteries [P. Masset and R. Guidotti, "Thermal activated (thermal) battery technology Part II. Molten salt electrolytes," J. Power Sources, vol. 164, pp. 397-414, 2007]. For heat treating applications, the chemical interaction of the present invention with
20 the heat treated metal should be understood in the relevant temperature range. For electrolyte applications, the ionic conductivity of the present invention should be measured as well as the compatibility with anode and cathode materials. Extensive data exists for binary and ternary phase diagrams of inorganic salts [Phase Diagrams for Ceramists, American Ceramic Society/NIST, vol. 1-4, 7, 1964-1989.]. However, there is minimal data available for
25 quaternary and higher order systems. This invention describes several useful quinary and higher order salt systems.

[0044] The compositions of the present invention can have any suitable melting point. The melting point can be, for example, less than about 300 °C, or less than about 250 °C, or less than about 150 °C, or less than about 100 °C. The melting point can be less than about 240,
30 230, 220, or 200 °C. In some embodiments, the composition has a melting point less than about 250 °C. In some embodiments, the composition has a melting point less than about 240 °C.

[0045] The compositions of the present invention can have any suitable thermal stability limit. The thermal stability limit can be, for example, greater than about 400 °C, or greater than about 450, 500, 550, 600, 650, or 700 °C. In some embodiments, the composition has a thermal stability limit greater than about 500 °C. In some embodiments, the composition has a thermal stability limit greater than about 565 °C. In some embodiments, the composition has a thermal stability limit greater than about 600 °C.

[0046] The compositions of the present invention can be prepared by any method known to one of skill in the art. For example, free-flowing anhydrous salt components can be prepared by grinding commercially available, reagent-grade salts with a mortar and pestle and dehydrating the ground salts in an oven. Salt mixtures can be formulated using automated equipment for measuring each component as it is being dispensed and recording the final weight of a given mixture. The mixtures can be dispensed in a suitable container, such as a glass well plate. Melting and homogenization of the mixtures can be conducted by heating the mixtures in a furnace under suitable conditions. The mixtures can be heated, for example, to 400 °C for 8 hours under nitrogen gas. The compositions can be stored with a desiccant until characterized and/or used.

[0047] The melting point of a mixture can be determined by heating a sample at a controlled rate and using an optical method to record the temperature at which each mixture transitions from opaque to clear. This transition corresponds to the liquidus temperature, which is defined as the temperature during heating at which the last remaining solid phase melts and becomes liquid. The liquidus temperature is also equivalent to the temperature during cooling at which a solid phase first appears in the melt.

[0048] Mixtures can also be characterized in terms of thermal stability. The thermal stability limit of a mixture can be measured using a thermogravimetric analysis (TGA) device. The TGA device heats a sample in a controlled environment and continuously measures the sample weight, which typically decreases at higher temperatures as the sample decomposes into gaseous products. The thermal stability limit of a sample can be assessed by determining the temperature at which it has lost a defined percentage of its anhydrous weight during a TGA temperature ramp. Testing can be conducted and compared under different atmospheres, such as a reactive atmosphere (*e.g.*, air) or an inert atmosphere (*e.g.*, nitrogen), in order to determine the effects of oxidation on the thermal stability limit.

IV. Methods of Storing and Transferring Thermal Energy

[0049] The compositions of the present invention are useful for collecting heat from an external source such as the sun. Accordingly, some embodiments of the present invention provide a method for storing solar thermal energy. The method includes exposing a composition as described above to sunlight. The compositions can be exposed directly or indirectly to sunlight. For example, sunlight can be focused using a lens or mirror and directed to a receiver containing the composition. The heat can be collected by the composition and transferred to water, causing the water to boil and generate steam for driving a turbine generator. The compositions can be useful in various systems for concentrating solar power that are known to one of skill in the art.

[0050] In some embodiments, the present invention provides a method for storing solar thermal energy includes exposing a composition to sunlight, wherein the composition contains: a sodium cation, in an amount of from about 55 to about 85 mol % based on the cations; a potassium cation, in an amount of from about 15 to about 40 mol % based on the cations; and a nitrate anion, in an amount of from about 75 to about 100 mol % based on the anions. The composition also contains at least one member selected from: a strontium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a barium cation, in an amount of from about 0.1 to about 10 mol % based on the cations; a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on the anions; and a chloride anion in an amount of from about 0.1 to about 15 mol % based on the anions.

[0051] In some embodiments, the present invention provides a method wherein the composition contains the sodium cation in the amount of from about 60 to about 65 mol % based on the cations; the potassium cation in the amount of from about 35 to about 40 mol % based on the cations; the nitrate anion in the amount of from about 90 to about 99 mol % based on the anions; the sulfate anion in the amount of from about 0 to about 3 mol % based on the anions; and the chloride anion in the amount of from about 0.1 to about 10 mol % based on the anions. In some embodiments, the present invention provides a method wherein the composition contains at least two members selected from the group consisting of the strontium cation, the barium cation, the sulfate anion, and the chloride anion.

V. Examples

[0052] The following examples are not intended to restrict the scope of the invention, but merely to illustrate possible embodiments.

General

[0053] Salt mixtures were formulated and characterized with an automated materials discovery workflow. The first step was to prepare free flowing anhydrous salt components. Components were purchased in reagent grade purity, typically 99% pure, from Sigma Aldrich (St. Louis, Missouri). Each component that was available in anhydrous form was ground with a mortar and pestle and dehydrated in an oven at 115°C for at least 12 hours. Salt mixtures were formulated using automated robotic systems for both powder dispensing and liquid dispensing. The powder dispensing system was the MTM Powdernium from Symyx Technologies (Sunnyvale, California). This device measures each component as it is being dispensed and records the final weight with high accuracy. It can dispense many different components to many different mixtures. The mixtures were dispensed into a borosilicate glass plate containing 96 wells in an 8 by 12 array. Each mixture had a total mass of 250 mg. After dispensing, the plate was placed in a furnace purged with nitrogen gas and heated to 400°C for at least 8 hours in order to ensure complete melting and homogenization of each mixture. After melting the plate was allowed to cool and stored in a desiccator until subsequent testing. The melting point of each mixture was measured with a Parallel Melting Point Workstation (PMP) from Symyx Technologies (Sunnyvale, California). The PMP allows the melting point for each mixture in the 96 well plate to be measured simultaneously. The PMP heats the plate at a controlled rate and uses an optical method to record the temperature at which each mixture transitions from opaque to clear. This transition corresponds to the liquidus temperature, which is defined as the temperature during heating at which the last remaining solid phase melts and becomes liquid. The liquidus temperature is also equivalent to the temperature during cooling at which a solid phase first appears in the melt (assuming no supercooling). However, supercooling is common with molten salts and therefore only data acquired during a heating mode was used to obtain the melting point. The melting point of a given composition was defined as its liquidus temperature.

[0054] The phase diagram is a graphical device that allows the composition and melting point of mixtures to be represented simultaneously. This type of phase diagram is called a polythermal projection. The typical phase diagram is triangular, which allows the plotting of a ternary system of three salts (typically four ions). Each corner of the triangle represents a pure ion and the interior area represents mixtures of varying proportions. The shade (*i.e.*, dark to light) represents the melting point. A quaternary system of four salts (typically five ions) may be plotted by a series of triangular phase diagrams (for diagrams for mixtures containing up to six ions, see Phase Diagrams for Ceramists, Vol. 1). The location of each

ternary diagram along a horizontal axis represents the proportion of the 5th ion. A quinary system of five salts (typically six ions) may be plotted by a two dimensional surface of ternary phase diagrams. Each ternary phase diagram is located at the (x, y) coordinates corresponding to the level of the 5th and 6th ions (ion 5, ion 6). A system of six salts
5 (typically seven ions) may be plotted by a series of two dimensional surfaces of ternary phase diagrams. Each surface represents a constant value of the 7th ion. The drawings included herein show representative phase diagrams from each of the major systems disclosed.

[0055] Mixtures that exhibited a low melting point were subjected to further testing for thermal stability. Approximately 20 mg of each mixture was scraped from its well in the
10 glass plate and loaded onto a platinum pan for testing. The thermal stability of mixtures was measured using a Q500 thermogravimetric analysis (TGA) device from TA Instruments (New Castle, Delaware). A TGA device heats a sample in a controlled environment and continuously measures the sample weight, which typically decreases at higher temperatures as the sample decomposes into gaseous products. The maximum temperature or thermal
15 stability of a sample, termed "T3," was defined for screening purposes as the temperature at which it has lost 3% of its anhydrous weight during a TGA test ramping at 10 °C/min. The anhydrous weight of a salt sample was defined as the weight at 300°C during the TGA test. Initial weight loss below 300°C is due to absorbed water evaporating from the sample. Each mixture was tested in two atmospheres, one of air and one of nitrogen, in order to observe the
20 effect of oxidation. The thermal stability using the T3 method typically produces similar results for each mixture in a given system; however significant differences are observed between systems. Therefore only a representative set of mixtures from each system were tested for thermal stability rather than every mixture in the system. Mixtures with only nitrate typically have similar T3 values for air and nitrogen atmospheres. The T3 method
25 ranks the mixtures in order of relative stability rather than acting as an absolute measurement of stability. It is a screening test that gives a comparative ranking of candidate salt mixtures.

Example 1

[0056] To prepare a laboratory scale salt mixture, 138.7 mg of NaNO₃, 80.2 mg of KNO₃, 16.9 mg of Sr(NO₃)₂, and 13.8 mg of Ba(NO₃)₂ was dispensed into a well on a borosilicate
30 glass plate.

[0057] The composition formula in this example is described by specifying the mass of each salt component, which can be translated to molar percent of each ion by those skilled in the art. A salt mixture of any desired size with the same properties (melting point and

thermal stability) can be prepared by increasing the amount of each component but maintaining the relative proportions. A formula with salt masses is given for simplicity but does not embody an exclusive method to achieve a given composition of ions; to exclusively describe a molten salt composition one must specify the ionic composition. For example, in a target ionic composition with several cations and with anions primarily of nitrate but with a minority of chloride, the chloride ion may be achieved by adding sodium chloride (NaCl) or potassium chloride (KCl) and adjusting the cations accordingly to achieve the equivalent ionic composition.

[0058] The mixture was heated in a furnace at a temperature of 400 °C for 8 hours to melt and homogenize the sample. The mixture was maintained at 115 °C after melting until it was removed from the furnace and allowed to cool to room temperature in a desiccator. A sample was inserted into the PMP Workstation and the temperature was set to 100 °C and allowed to stabilize for 60 minutes. The temperature was then ramped to 315 °C at 20 °C/hour. After measuring the melting point, 20 mg of the sample was removed and placed onto a platinum pan. The pan was loaded into the thermogravimetric analysis (TGA) apparatus and the temperature was ramped from ambient to 700 °C at 10°C/min using air as the purge gas. The TGA test was repeated with another 20 mg from the sample using nitrogen as the purge gas. Phase diagrams showing melting point data for compositions ranges including Example 1 are shown in Figure 1. The melting point of Example 1 was 245 °C, as measured with the PMP (Table 2). The thermal stability results for Example 1 can be seen in Table 2. TGA data recorded for Example 1 in air and nitrogen are shown in Figure 2 and Figure 3, respectively.

Examples 2-27

[0059] Further examples of each system are summarized below in Table 1 and Table 2. The composition of each is expressed in molar percent on an ion basis, which can be converted to weight percent by those skilled in the art. The melting point and the maximum temperature in air and nitrogen are expressed in degrees Celsius. Several methods were used to measure the melting point, including the PMP (Parallel Melting Point Workstation), DSC (differential scanning calorimeter), MPA (Melting Point Apparatus, visual test with a small sample in capillary tube), and a visual beaker test in a furnace.

Table 1: Composition of Examples

Example	Composition (mol %)						
	Na	K	Sr	Ba	NO3	SO4	Cl
1	63.8%	31.0%	3.1%	2.1%	100.00%		
2	63.7%	30.0%	5.2%	1.0%	100.00%		
3	64.1%	30.9%	3.9%	1.1%	100.00%		
4	75.6%	24.4%			88.3%	7.6%	4.1%
5	75.0%	25.0%			91.6%	4.4%	4.0%
6	75.0%	25.0%			88.3%	2.0%	9.7%
7	65.5%	30.5%	4.1%		94.1%		5.9%
8	64.9%	33.0%	2.1%		94.1%		5.9%
9	65.0%	30.9%	4.1%		96.0%		4.0%
10	65.4%	32.5%		2.1%	93.8%		6.2%
11	64.5%	33.4%		2.1%	95.9%		4.1%
12	65.0%	33.1%		1.9%	97.2%		2.8%
13	71.0%	24.7%	3.2%	1.1%	100.00%		
14	71.0%	25.7%	2.1%	1.2%	100.00%		
15	68.2%	27.8%	4.0%		93.9%		6.1%
16	70.3%	27.7%	2.0%		95.1%		4.9%
17	70.5%	25.5%	4.0%		97.4%		2.6%
18	73.2%	24.8%		2.0%	91.0%		9.0%
19	72.9%	23.1%		4.1%	93.1%		6.9%
20	71.2%	24.8%		4.0%	92.2%		7.8%
21	69.4%	23.9%	4.1%	2.5%	93.9%		6.1%
22	69.8%	27.0%	2.2%	1.1%	92.0%		8.0%
23	69.8%	27.0%	2.0%	1.2%	93.8%		6.2%

Table 2: Melting Point and Thermal Stability Data of Salt Compositions

Example	Melting Point (°C)				Thermal Stability (°C)	
	PMP	DSC	MPA	Beaker	Air T3	N2 T3
1	245.2	234.3	246		624.4	600.4
2	249.0	236.2	246		630.3	613.4
3	246.9	237.3	242		630.8	609.2
4	243.3	232.1	243		639.9	633.4
5	248.8	234.8			647.0	634.1
6	247.5	238.4			652.0	643.7
7	238.9	231.7	240		631.1	620.2
8	236.9	226.0	238		635.7	622.1
9	237.2	240.7			630.7	610.9
10	236.5	229.1	239		629.8	612.9
11	238.1	226.9	230		634.0	614.1
12	241.4	226.9	232		627.6	467.4
13	248.1	241.7	245		628.9	620.5
14	249.5	247.9	251		634.0	624.9
15	248.9	235.2			646.6	632.8
16	248.3	238.4			638.3	619.8
17	248.0	240.0			649.5	614.5
18	249.0	243.5			645.9	625.1
19	248.5	241.5			635.9	617.7
20	245.6	237.6			631.1	617.7
21	244.3	239.3			627.9	609.6
22	242.3	233.4	250		617.7	624.6
23	243.2	236.5				

[0060] Data for further Examples 24-27 is presented in Table 3 below.

Table 3: Content and Physical Properties of Salt Compositions

Example	Composition (mol%)					Melting Point (°C)		Thermal Stability (°C)	
	Na	K	SO4	Cl	NO3	PMP	DSC	N2 T3	Air T3
24	65.1%	34.9%	0.0%	4.2%	95.8%	242.25	237	622	643
25	65.0%	35.0%	2.1%	1.9%	96.0%	239.15	235	632	639
26	65.4%	34.6%	2.2%	4.5%	93.4%	234.15	231	632	638
27	60.2%	39.8%		6.1%	93.9%		216	613	655

5

[0061] Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, one of skill in the art will appreciate that certain changes and modifications may be practiced within the scope of the appended claims. In addition, each reference provided herein is incorporated by reference in its entirety to the same extent as if each reference was individually incorporated by reference. Where a conflict exists between the instant application and a reference provided herein, the instant application shall dominate.

10

WHAT IS CLAIMED IS:

- 1 1. A composition comprising:
2 a sodium cation, in an amount of from about 55 to about 85 mol % based on the
3 cations;
4 a potassium cation, in an amount of from about 15 to about 40 mol % based on the
5 cations;
6 a nitrate anion, in an amount of from about 75 to about 100 mol % based on the
7 anions; and
8 at least two members selected from the group consisting of:
9 a strontium cation, in an amount of from about 0.1 to about 10 mol % based on
10 the cations,
11 a barium cation, in an amount of from about 0.1 to about 10 mol % based on
12 the cations,
13 a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on
14 the anions, and
15 a chloride anion in an amount of from about 0.1 to about 15 mol % based on
16 the anions.
- 1 2. A composition consisting essentially of:
2 a sodium cation, in an amount of from about 55 to about 85 mol % based on the
3 cations;
4 a potassium cation, in an amount of from about 15 to about 40 mol % based on the
5 cations;
6 a nitrate anion, in an amount of from about 75 to about 100 mol % based on the
7 anions; and
8 at least two members selected from the group consisting of:
9 a strontium cation, in an amount of from about 0.1 to about 10 mol % based on
10 the cations,
11 a barium cation, in an amount of from about 0.1 to about 10 mol % based on
12 the cations,
13 a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on
14 the anions, and
15 a chloride anion in an amount of from about 0.1 to about 15 mol % based on
16 the anions.

- 1 3. The composition of claim 1 or claim 2, wherein the composition
2 comprises the strontium cation and the barium cation.
- 1 4. The composition of claim 1 or claim 2, wherein the composition
2 comprises the sulfate anion and the chloride anion.
- 1 5. The composition of claim 1 or claim 2, wherein the composition
2 comprises the strontium cation and the chloride anion.
- 1 6. The composition of claim 1 or claim 2, wherein the composition
2 comprises the barium cation and the chloride anion.
- 1 7. The composition of claim 1 or claim 2, wherein the composition
2 comprises the strontium cation and the sulfate anion.
- 1 8. The composition of claim 1 or claim 2, wherein the composition
2 comprises the barium cation and the sulfate anion.
- 1 9. The composition of claim 1 or claim 2, wherein the composition
2 comprises at least three members selected from the group consisting of the strontium cation,
3 the barium cation, the sulfate anion, and the chloride anion.
- 1 10. The composition of claim 9, wherein the composition comprises the
2 strontium cation, the barium cation, and the chloride anion.
- 1 11. The composition of claim 9, wherein the composition comprises the
2 strontium cation, the barium cation, and the sulfate anion.
- 1 12. The composition of claim 9, wherein the composition comprises the
2 barium cation, the sulfate anion, and the chloride anion.
- 1 13. The composition of claim 1 or claim 2, wherein the composition
2 comprises the strontium cation, the barium cation, the sulfate anion, and the chloride anion.
- 1 14. The composition of claim 1, comprising:
2 the sodium cation in the amount of about 65 mol % based on the cations;
3 the potassium cation in the amount of about 35 mol % based on the cations;
4 the nitrate anion in the amount of from about 92 to about 97 mol % based on the
5 anions;

6 the sulfate anion in the amount of about 2 mol % based on the anions;
7 and the chloride anion in the amount of from about 1 to about 5 mol % based on the
8 anions.

1 15. The composition of claim 1, comprising:
2 the sodium cation in the amount of from about 64 to about 66 mol % based on the
3 cations;
4 the potassium cation in the amount of from about 30 to about 34 mol % based on the
5 cations;
6 the strontium cation in the amount of from about 2 to about 5 mol % based on the
7 anions;
8 the nitrate anion in the amount of from about 94 to about 96 mol % based on the
9 anions;
10 and the chloride anion in the amount of from about 4 to about 6 mol % based on the
11 anions.

1 16. The composition of claim 1, comprising:
2 the sodium cation in the amount of from about 68 to about 71 mol % based on the
3 cations;
4 the potassium cation in the amount of from about 25 to about 28 mol % based on the
5 cations;
6 the strontium cation in the amount of from about 2 to about 4 mol % based on the
7 anions;
8 the nitrate anion in the amount of from about 93 to about 98 mol % based on the
9 anions;
10 and the chloride anion in the amount of from about 2 to about 7 mol % based on the
11 anions.

1 17. The composition of claim 1, comprising:
2 the sodium cation in the amount of from about 64 to about 66 mol % based on the
3 cations;
4 the potassium cation in the amount of from about 32 to about 34 mol % based on the
5 cations;
6 the barium cation in the amount of about 2 mol % based on the anions;
7 the nitrate anion in the amount of from about 93 to about 97 mol % based on the
8 anions;

9 and the chloride anion in the amount of from about 2 to about 7 mol % based on the
10 anions.

1 18. The composition of claim 1, comprising:
2 the sodium cation in the amount of from about 71 to about 73 mol % based on the
3 cations;
4 the potassium cation in the amount of from about 23 to about 25 mol % based on the
5 cations;
6 the barium cation in the amount of from about 2 to about 4 mol % based on the
7 anions;
8 the nitrate anion in the amount of from about 91 to about 93 mol % based on the
9 anions;
10 and the chloride anion in the amount of from about 7 to about 9 mol % based on the
11 anions.

1 19. The composition of claim 1, comprising:
2 the sodium cation in the amount of about 69 mol % based on the cations;
3 the potassium cation in the amount of from about 24 to about 27 mol % based on the
4 cations;
5 the strontium cation in the amount of from about 2 to about 4 mol % based on the
6 anions;
7 the barium cation in the amount of from about 1 to about 3 mol % based on the
8 anions;
9 the nitrate anion in the amount of from about 92 to about 94 mol % based on the
10 anions;
11 and the chloride anion in the amount of from about 6 to about 8 mol % based on the
12 anions.

1 20. A method for storing solar thermal energy comprising exposing a
2 composition to sunlight, wherein the composition comprises:
3 a sodium cation, in an amount of from about 55 to about 85 mol % based on the
4 cations;
5 a potassium cation, in an amount of from about 15 to about 40 mol % based on the
6 cations;
7 a nitrate anion, in an amount of from about 75 to about 100 mol % based on the
8 anions; and

9 at least one member selected from the group consisting of:
10 a strontium cation, in an amount of from about 0.1 to about 10 mol % based on
11 the cations,
12 a barium cation, in an amount of from about 0.1 to about 10 mol % based on
13 the cations,
14 a sulfate anion, in an amount of from about 0.1 to about 15 mol % based on
15 the anions, and
16 a chloride anion in an amount of from about 0.1 to about 15 mol % based on
17 the anions.

1 21. The method of claim 20, wherein the composition comprises
2 the sodium cation in the amount of from about 60 to about 65 mol % based on the
3 cations;
4 the potassium cation in the amount of from about 35 to about 40 mol % based on the
5 cations;
6 the nitrate anion in the amount of from about 90 to about 99 mol % based on the
7 anions;
8 the sulfate anion in the amount of from about 0 to about 3 mol % based on the anions;
9 and the chloride anion in the amount of from about 0.1 to about 10 mol % based on
10 the anions.

1 22. The method of claim 20, wherein the composition comprises at least
2 two members selected from the group consisting of the strontium cation, the barium cation,
3 the sulfate anion, and the chloride anion.

1 / 5

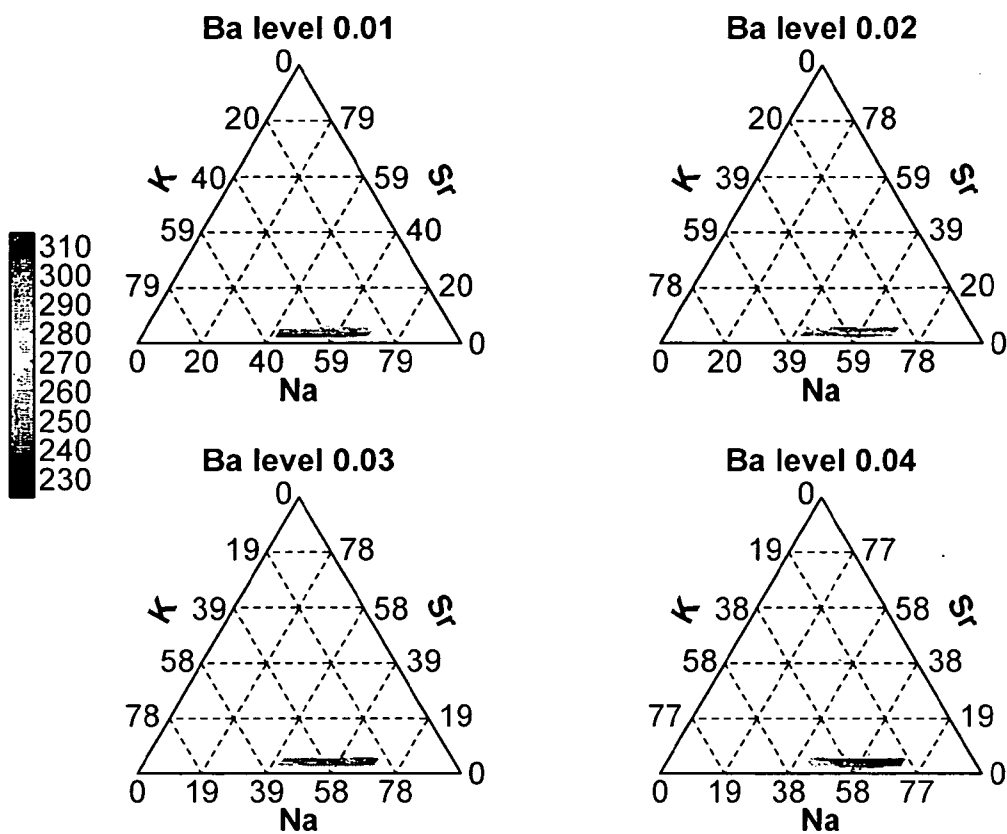


FIG. 1

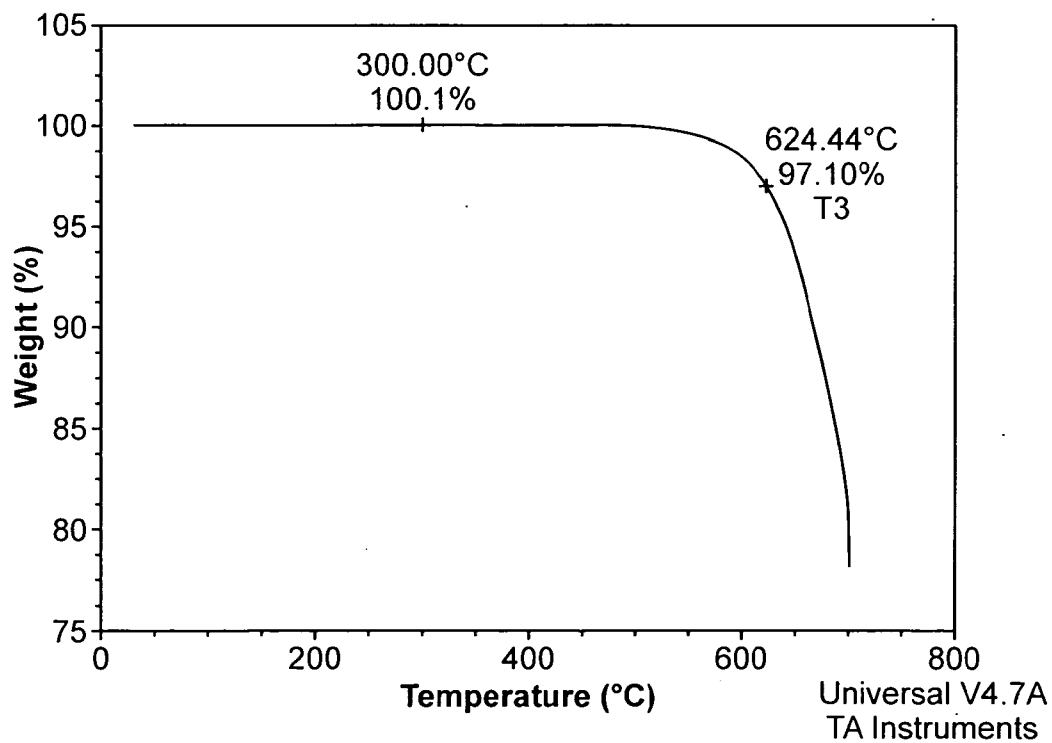


FIG. 2

2 / 5

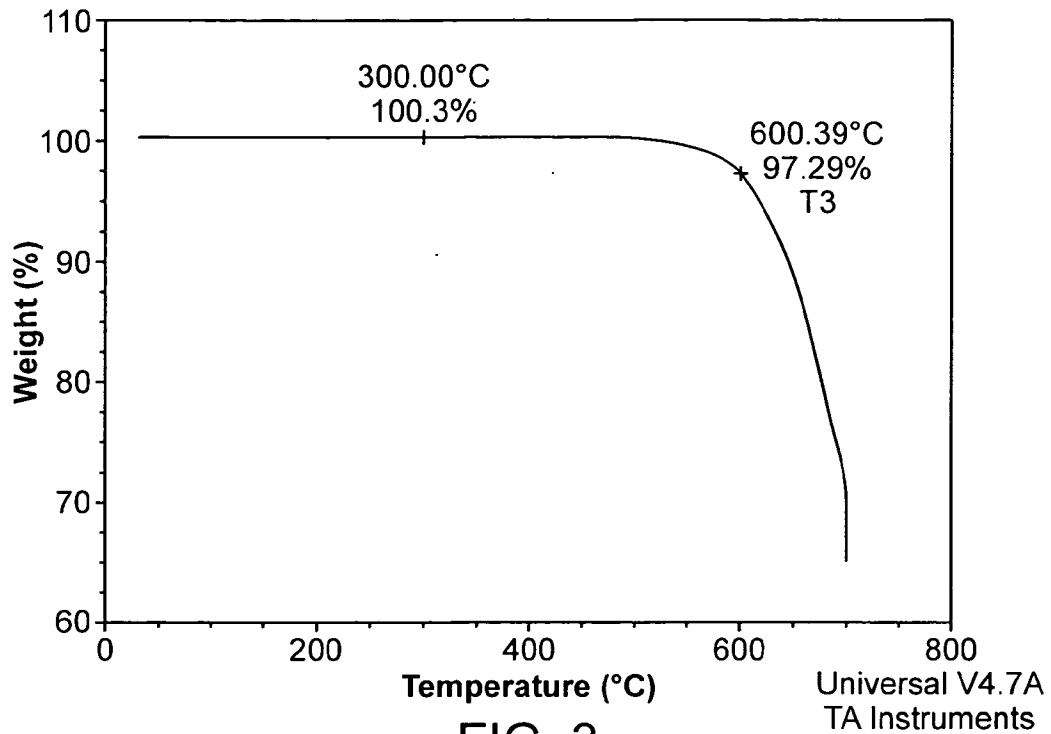


FIG. 3

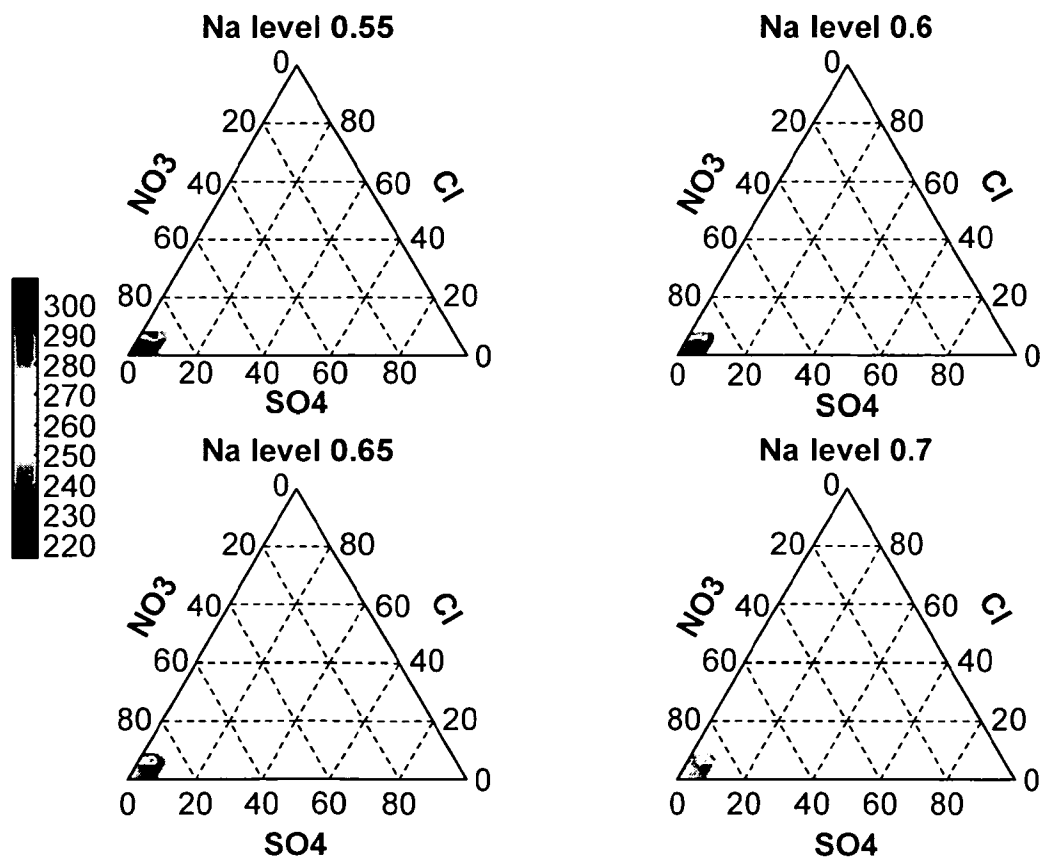


FIG. 4

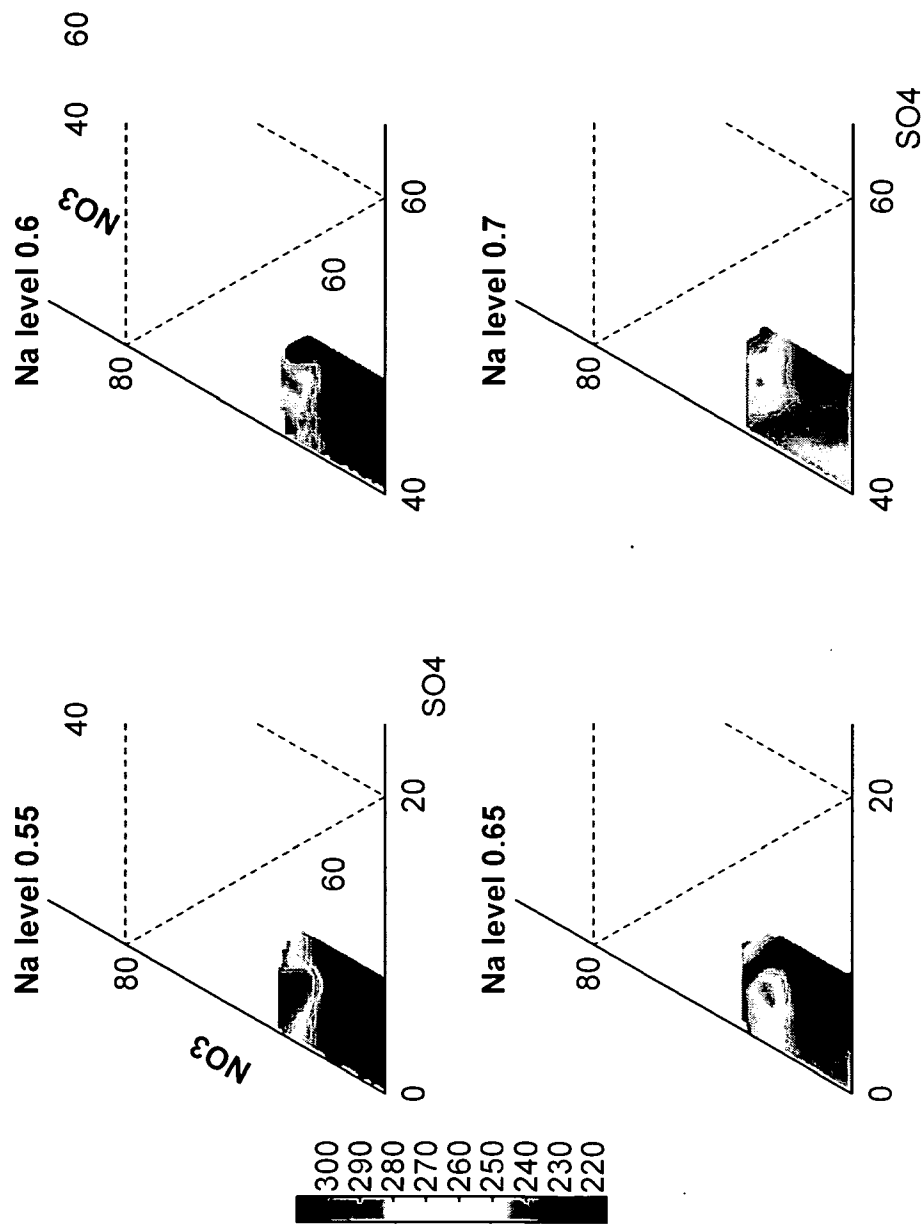


FIG. 5

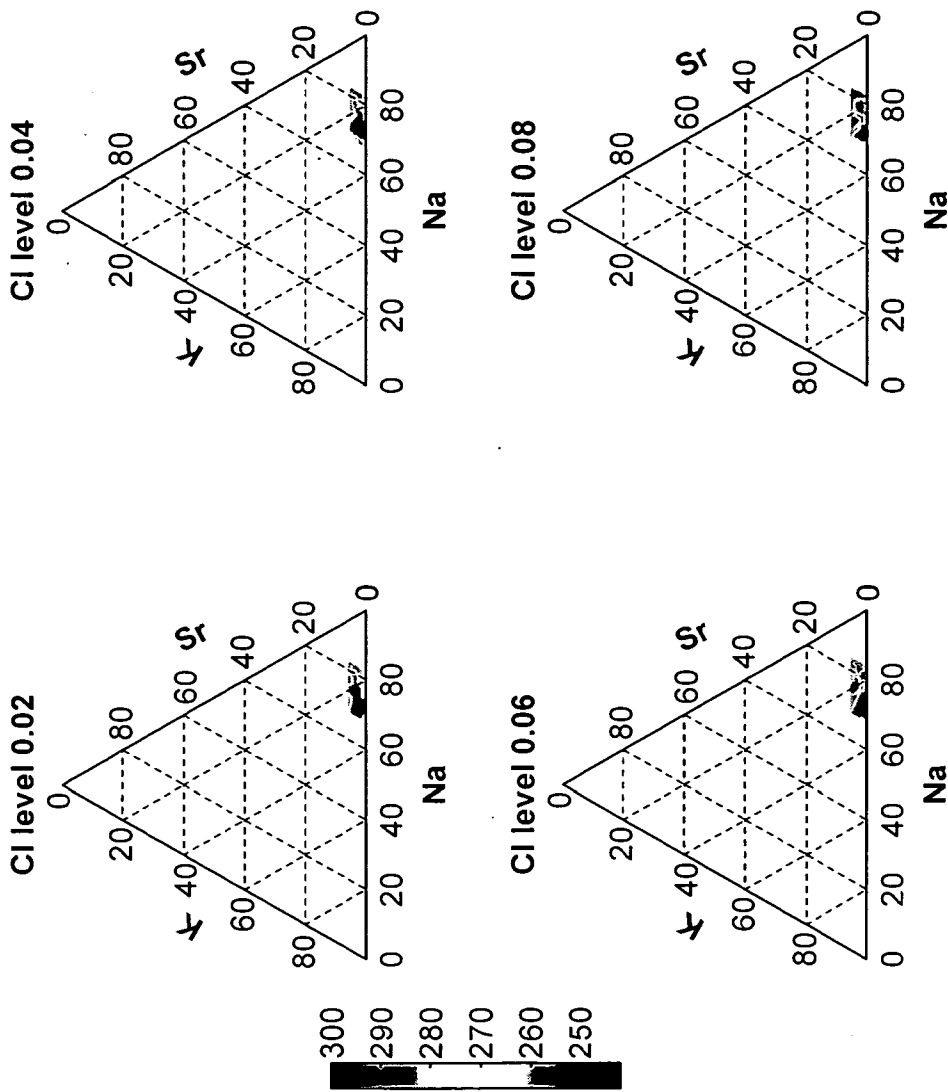


FIG. 6

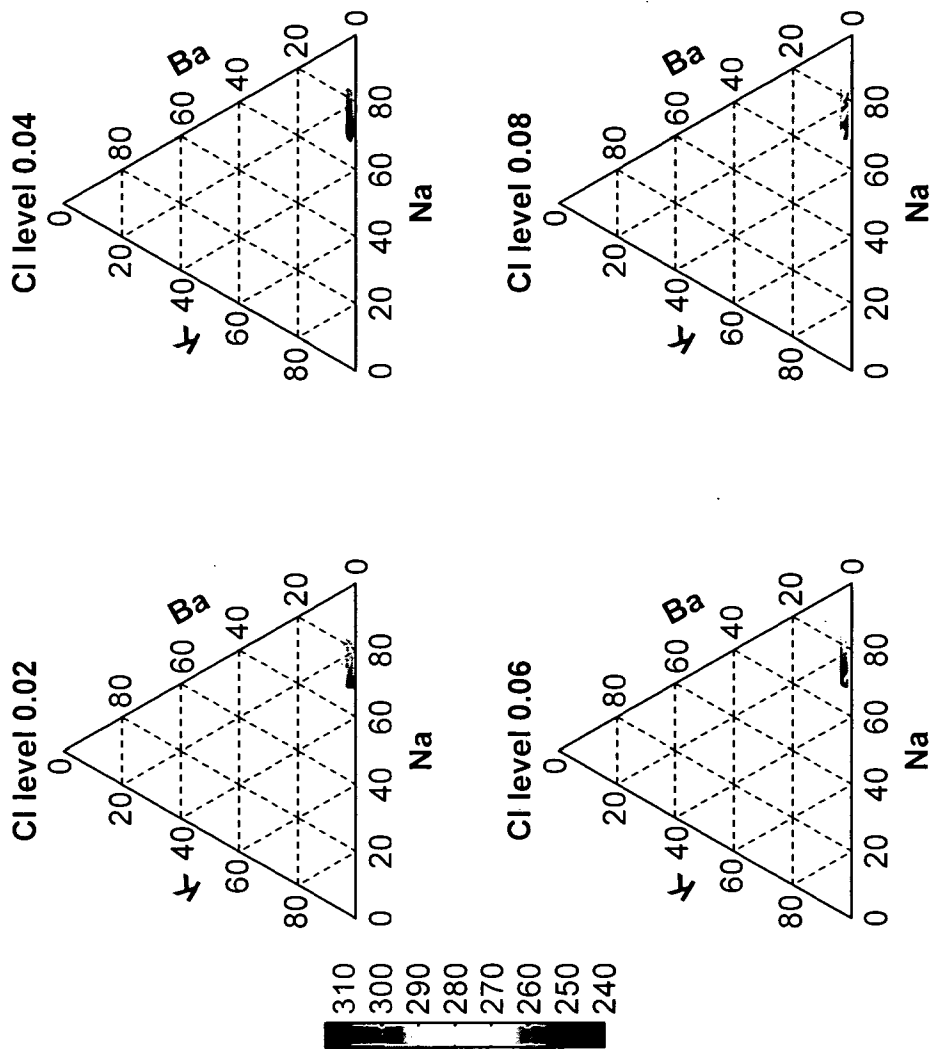


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/37808

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09K 5/00; C09K 5/06 (2012.01)

USPC - 252/70; 149/41; 149/61; 23/293A; 23/293R

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)
USPC - 252/70

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 252/70; 149/41; 149/61; 23/293A; 23/293R (text search - see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Google Patent, Google Scholar, PGPUB, USPT
Search terms used: molten, salt, heat, transfer, fluid, thermal, sodium, potassium, nitrate, sulfate, chloride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0211726 A1 (Bank et al.) 27 August 2009 (27.08.2009); entire document, especially paras. [0034] and [0052]-[0057]	1-22
Y	US 5,567,346 A (Kakiuchi et al.) 22 October 1996 (22.10.1996); entire document, especially col. 2, ln. 28, 29, and 56-58; col. 2, ln. 32-33; col. 3, ln. 20-22; and col. 2, ln. 29-30, 67 to col. 3, ln. 3	1-22
Y	US 4,119,556 A (Chubb) 10 October 1978 (10.10.1978); entire document, especially col. 2, ln. 36-44	3, 5-13, 15-19

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

* Special categories of cited documents:

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"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

16 July 2012 (16.07.2012)

Date of mailing of the international search report

09 AUG 2012

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