



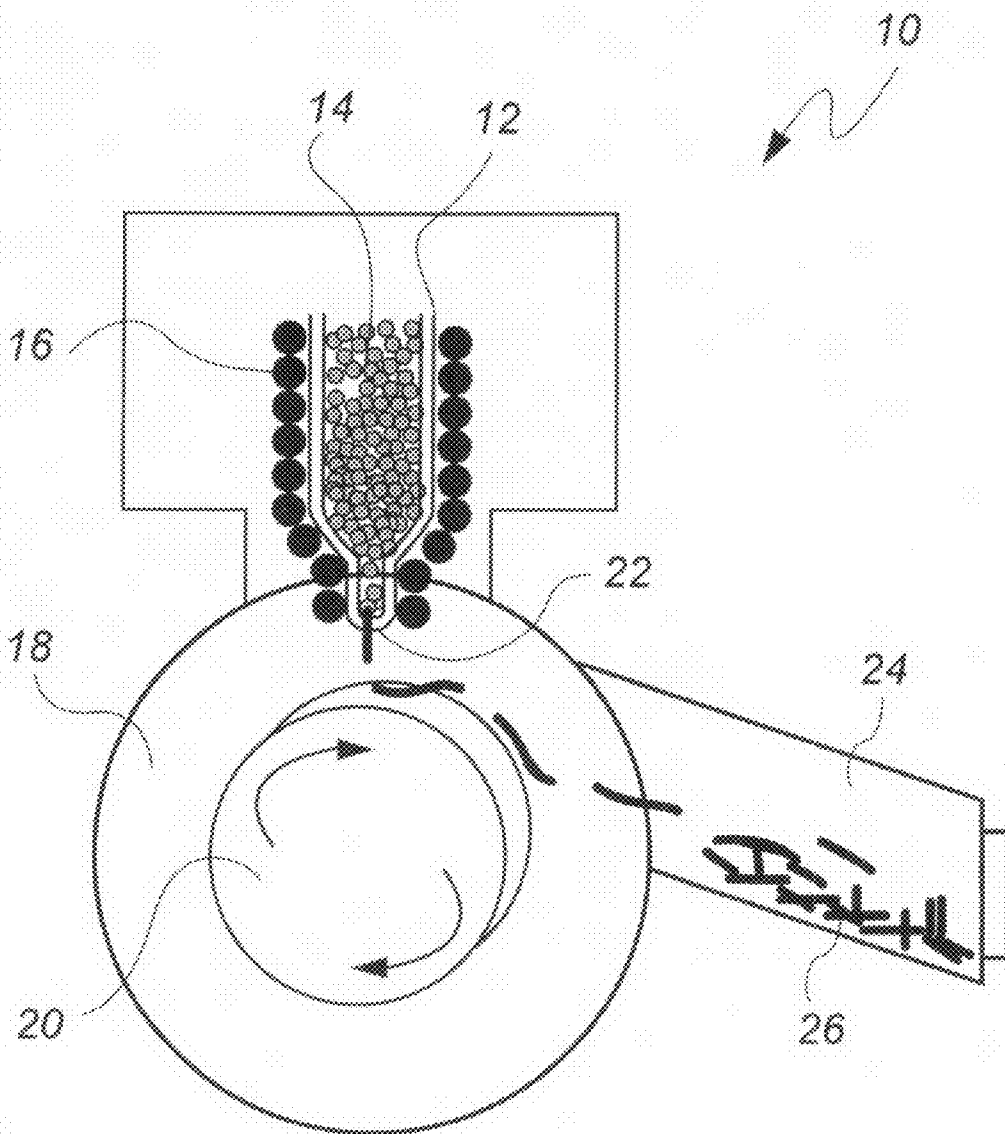
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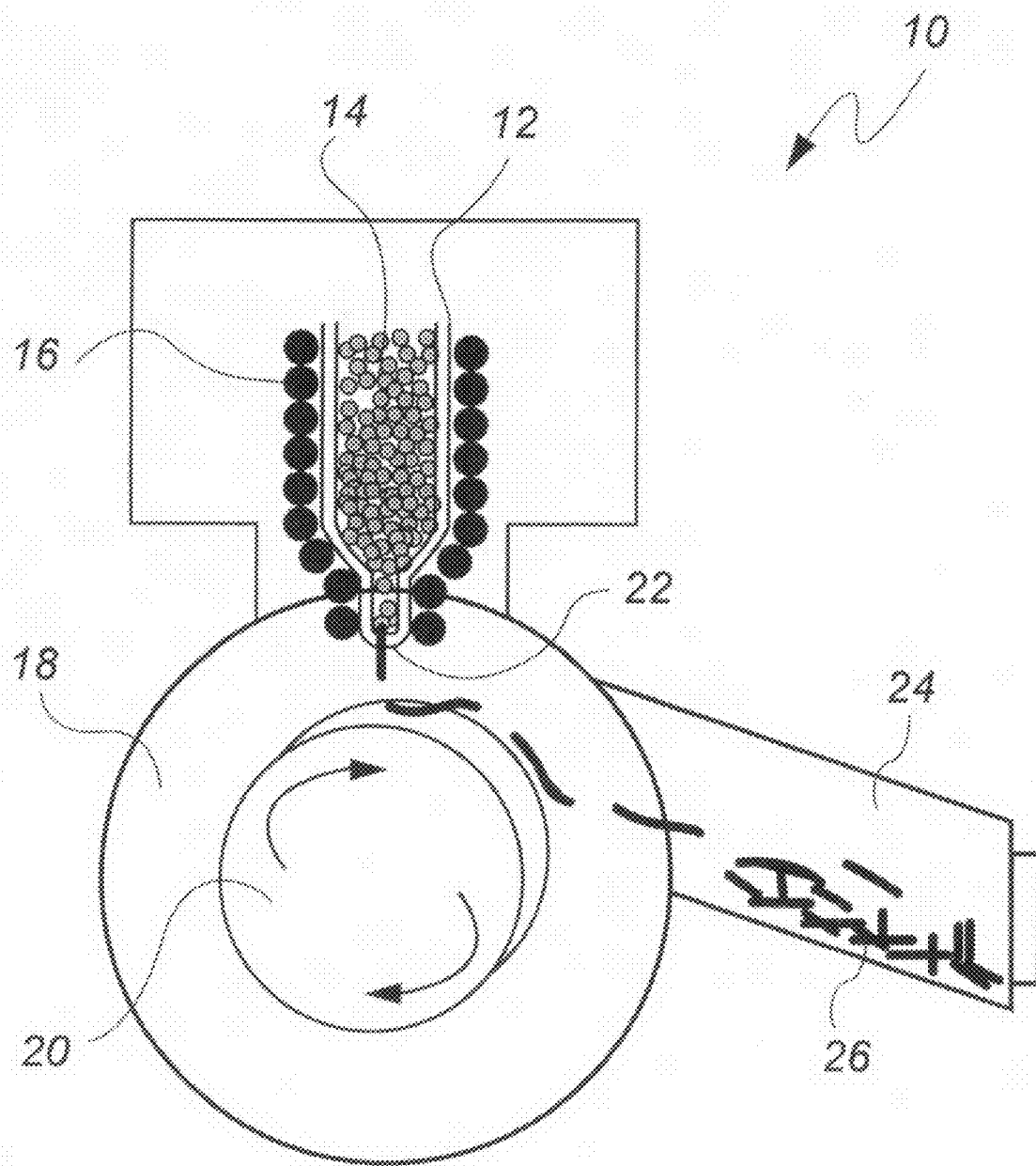
(19) **United States**(12) **Patent Application Publication**  
**Chen et al.**(10) **Pub. No.: US 2008/0185074 A1**(43) **Pub. Date: Aug. 7, 2008**(54) **PREPARATION OF COMPOSITIONS BY  
MELT SPINNING**(75) Inventors: **Ching-Fong Chen**, Los Alamos,  
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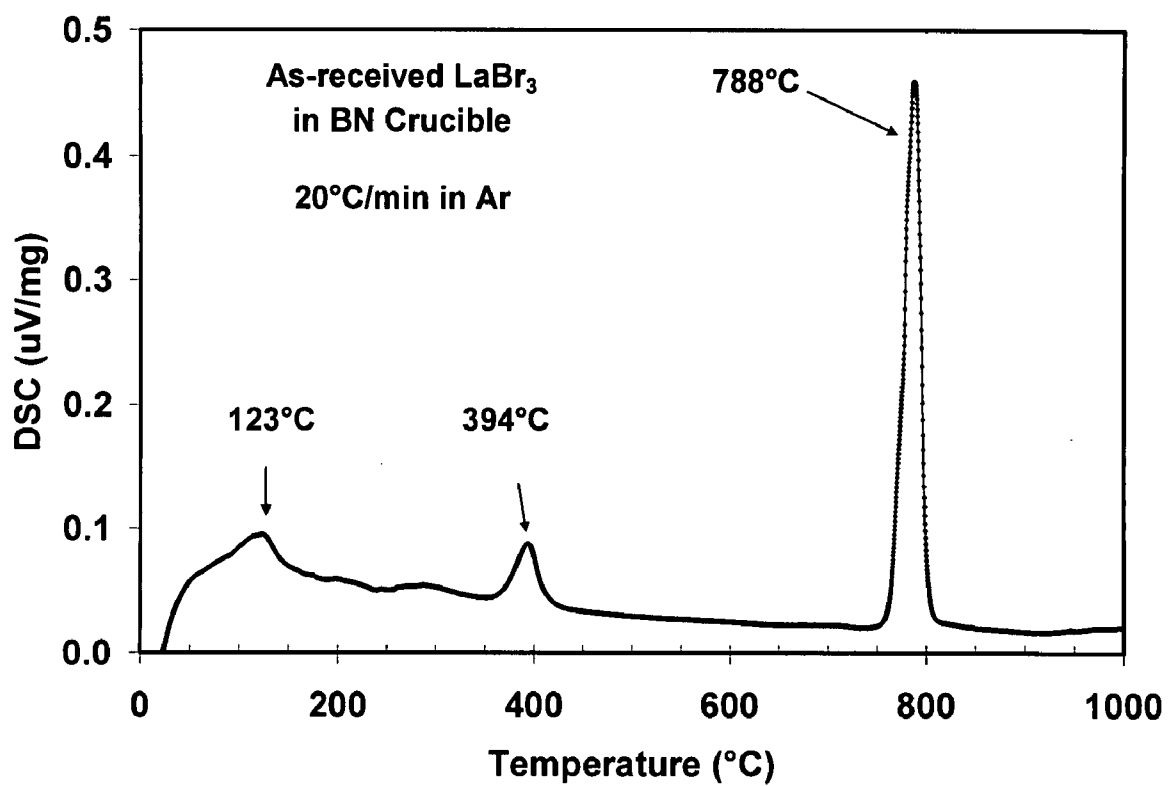
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**B22F 1/00** (2006.01)(52) **U.S. Cl.** ..... **148/513; 148/317**(57) **ABSTRACT**

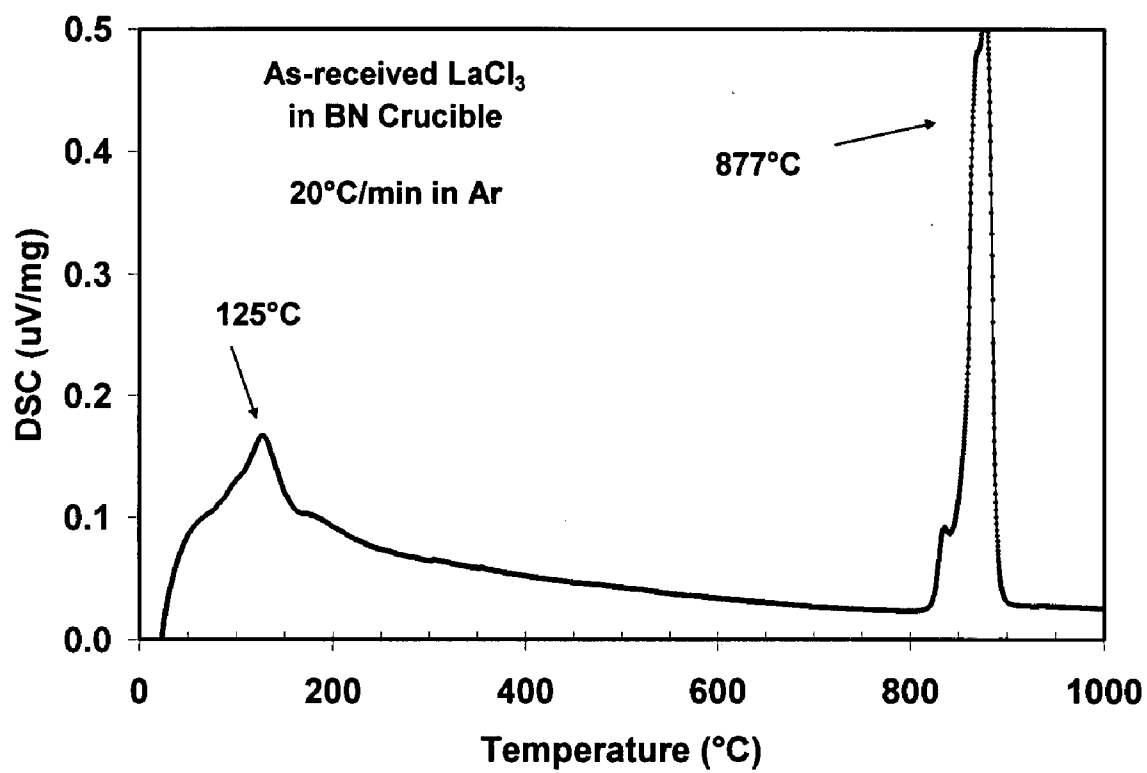
Inorganic compositions were prepared by melt spinning. An inorganic melt was sent to a spinning wheel. As the melt contacts the wheel, it cools and is converted into a solid composition. A melt prepared from lanthanum halide powder and cerium halide powder was converted to a scintillator product of nanoparticles embedded in a glassy matrix.



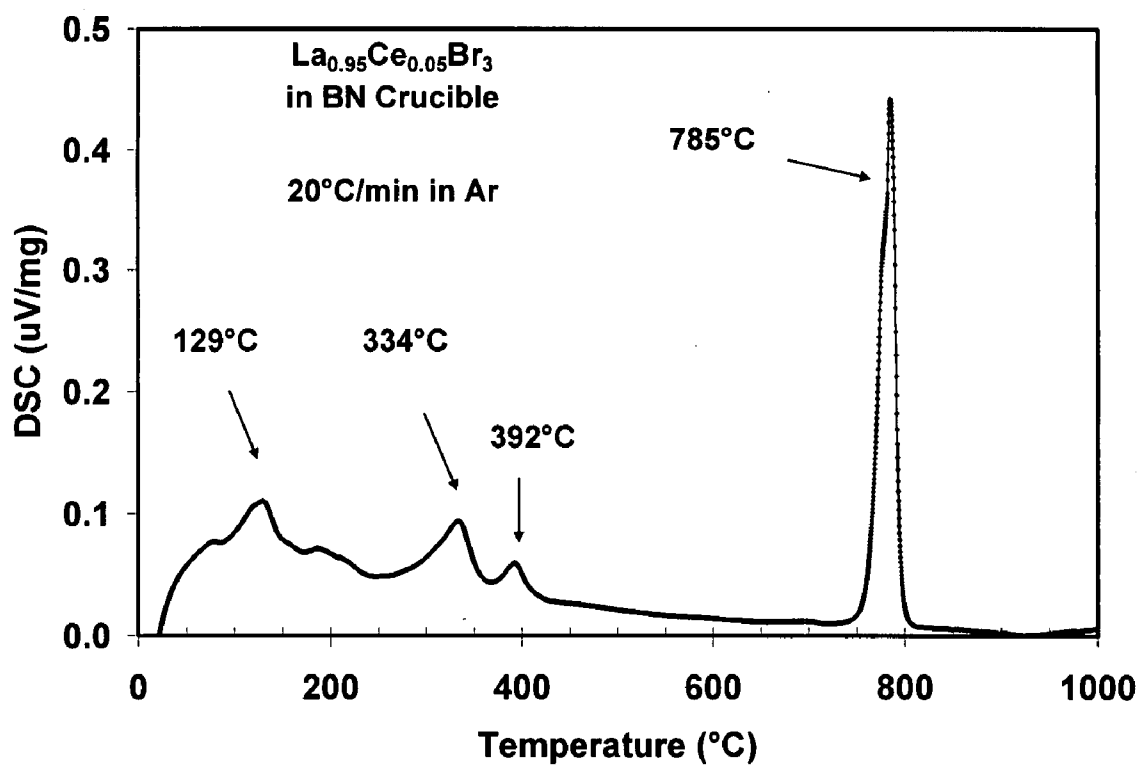


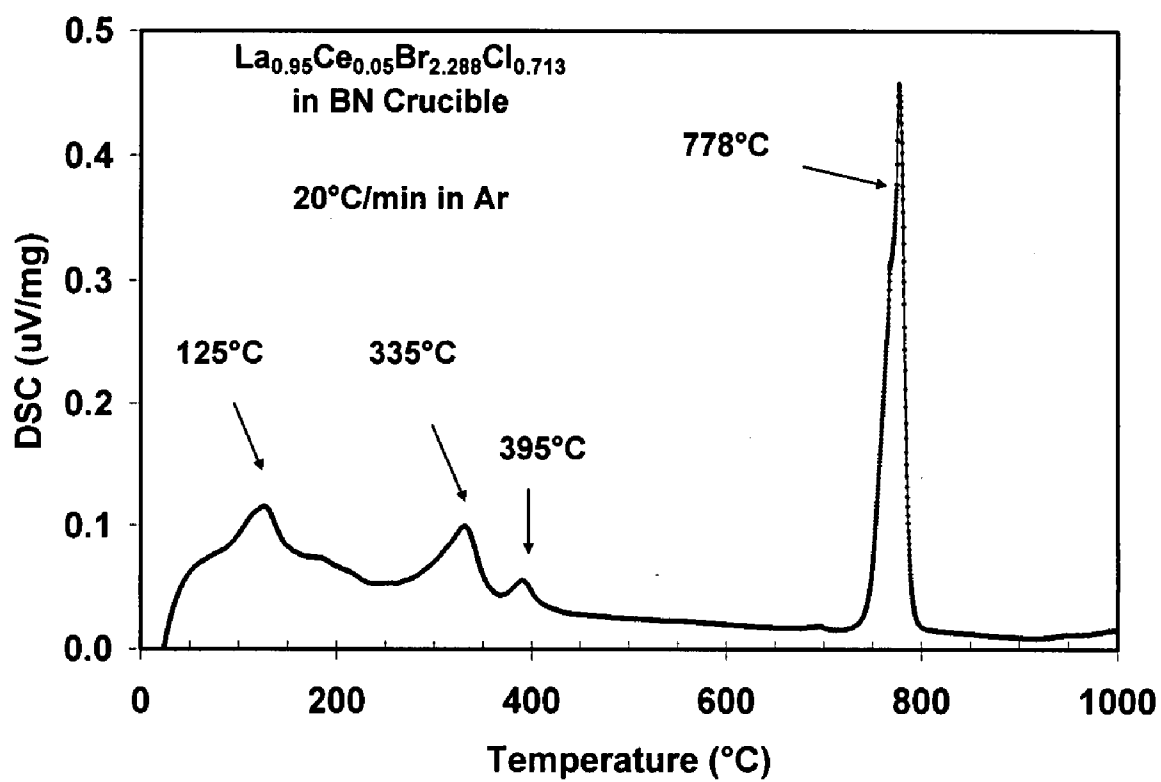
**Fig. 1**

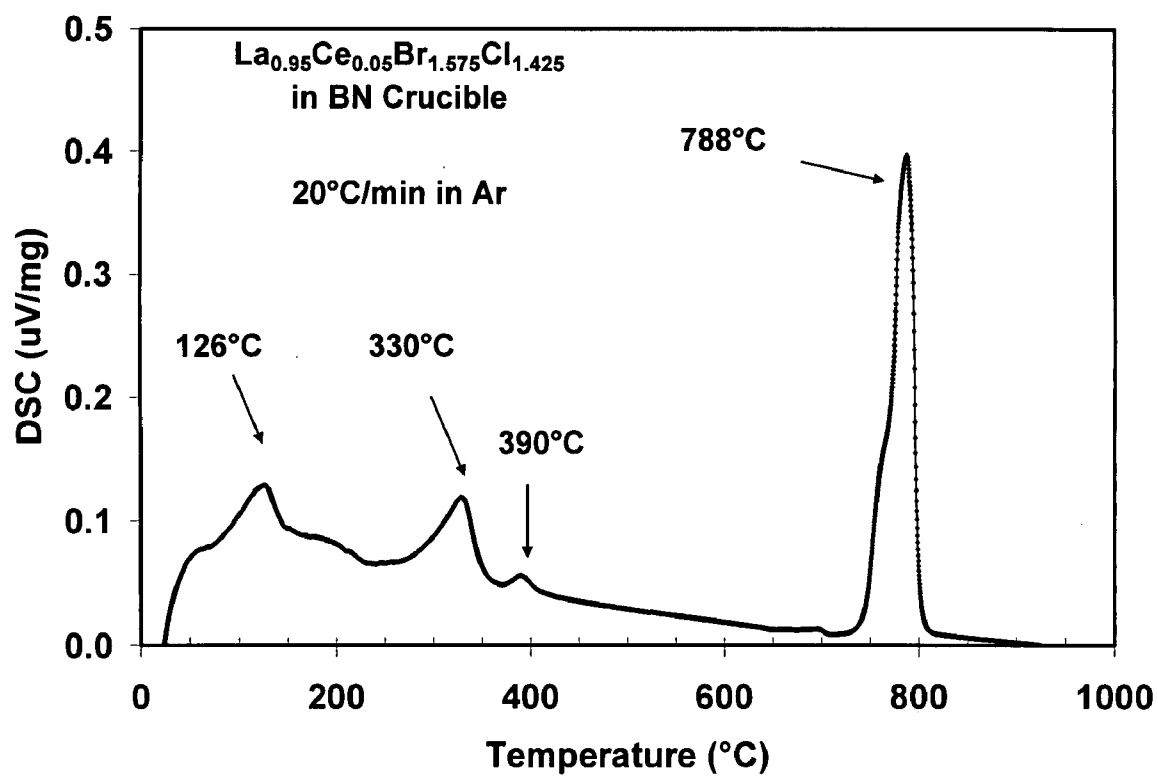
**Fig. 2**

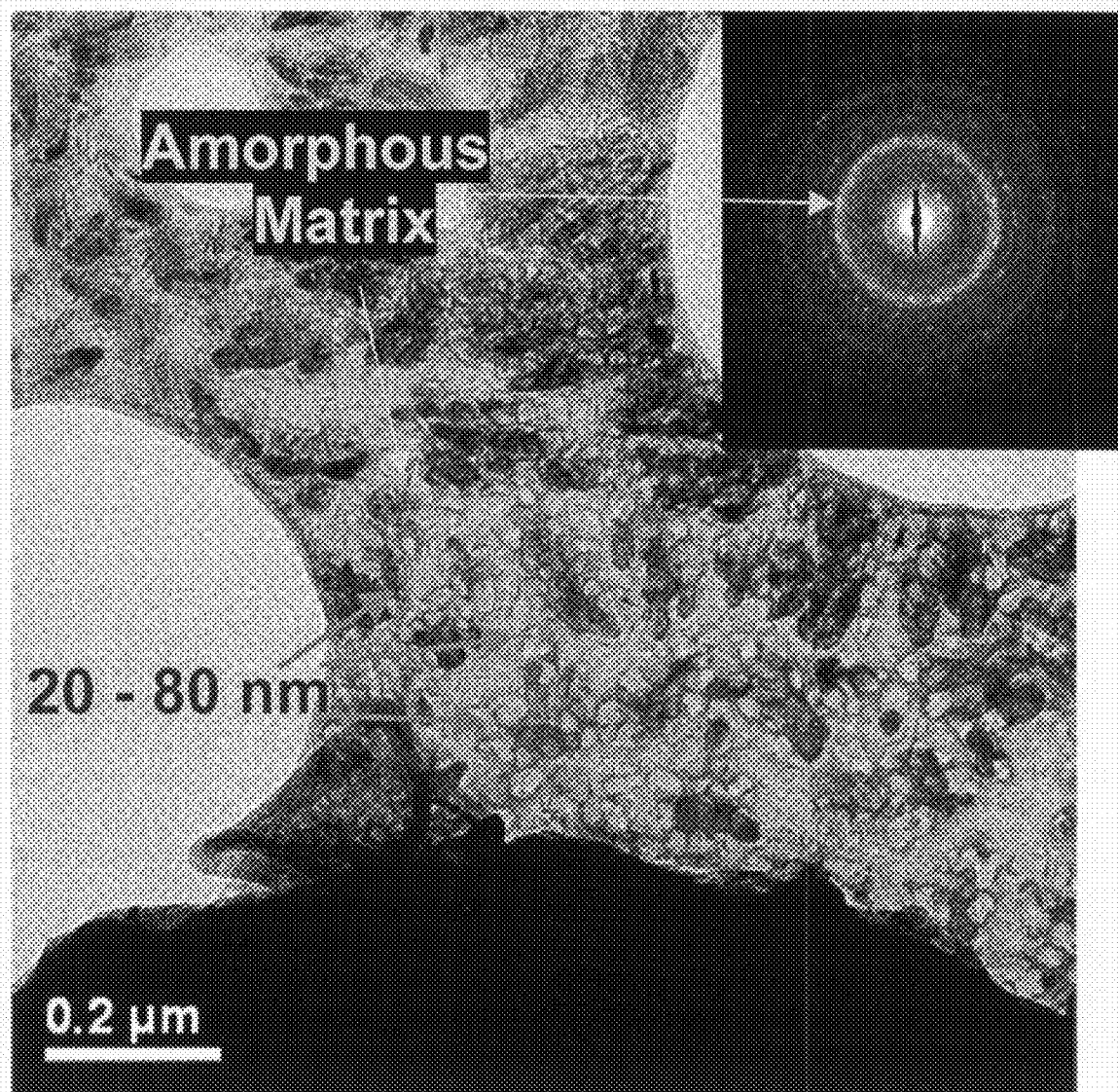


***Fig. 3***

**Fig. 4**

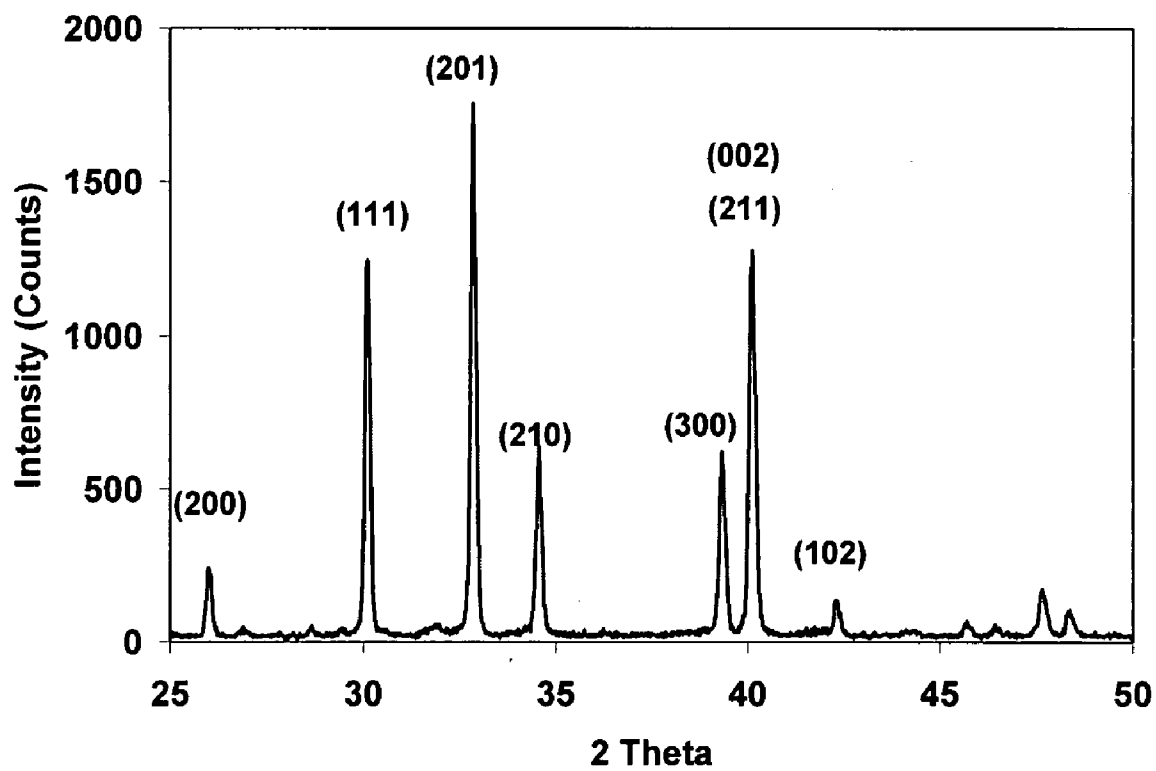
**Fig. 5**

**Fig. 6**



*Fig. 7*





**Fig. 8**

## PREPARATION OF COMPOSITIONS BY MELT SPINNING

### STATEMENT REGARDING FEDERAL RIGHTS

[0001] This invention was made with government support under Contract No. DE-AC51-06NA25396 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

### FIELD OF THE INVENTION

[0002] The invention relates to the preparation of inorganic compositions by melt spinning.

### BACKGROUND OF THE INVENTION

[0003] Nanostructured materials generally have different electronic, magnetic, optical, and mechanical properties than the corresponding bulk materials. Light output from nanophosphors, for example, can be higher than for micron-sized or larger phosphors. Nanophosphors have attracted interest due to their potential uses in optics, optoelectronics, lighting, displays, optical amplifiers/scintillators, lasers, microelectronics, tribology, homeland security, radiation detectors, medical imaging, and other applications.

[0004] There remains a need for better methods for preparing nanostructured materials.

### SUMMARY OF THE INVENTION

[0005] In accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention is concerned with a process for preparing a composition. The process includes sending an inorganic melt to a spinning wheel, whereby the melt cools after it contacts the wheel and is converted into a product that comprises nanoparticles embedded in a glassy matrix.

[0006] The present invention is also concerned with a product prepared by a process that comprises sending an inorganic melt to a spinning wheel that cools the melt after the melt contacts the spinning wheel, whereby the melt is converted into a product that comprises nanoparticles of a composition embedded in a glassy matrix of essentially the same composition.

[0007] The present invention is also concerned with a composition that consists essentially of nanoparticles of a composition embedded in a glassy matrix of essentially the same composition as that of the nanoparticles.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The accompanying drawings, which are incorporated in and form a part of the specification, illustrate embodiments of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

[0009] FIG. 1 shows a schematic representation demonstrating operating principles of a melt spinner.

[0010] FIG. 2 shows results from a differential scanning calorimeter (DSC) run for lanthanum bromide ( $\text{LaBr}_3$ ) powder.

[0011] FIG. 3 shows results from a DSC run for lanthanum chloride ( $\text{LaCl}_3$ ) powder.

[0012] FIG. 4 shows results from a DSC run for a powder mixture having the formula  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$  powder.

[0013] FIG. 5 shows results from a DSC run for a powder mixture having the formula  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$  powder.

[0014] FIG. 6 shows results from a DSC run for a powder mixture having the formula  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{1.575}\text{Cl}_{1.425}$  powder.

[0015] FIG. 7 shows a transmission electron microscope (TEM) micrograph showing the microstructure of an embodiment flake of nanoparticles embedded in a glassy matrix of the invention.

[0016] FIG. 8 shows an x-ray diffraction (XRD) pattern of an embodiment phase of  $\text{LaBr}_3\text{:Ce}$  nanoparticles.

### DETAILED DESCRIPTION

[0017] The present invention provides compositions and methods for preparing the compositions. The compositions are generally inorganic compositions. Some embodiments of these compositions are phosphors.

[0018] Some non-limiting embodiment compositions of the invention include rare earth doped lanthanum fluoride, rare earth doped lanthanum chloride, rare earth doped lanthanum bromide, and rare earth doped mixtures of lanthanum chloride and lanthanum bromide. Some non-limiting embodiment rare earth dopants include cerium, neodymium, europium, thulium, terbium, samarium, gadolinium, dysprosium, and praseodymium. Some other non-limiting embodiment dopants include thallium, chromium, manganese, titanium, copper, silver, zinc, gallium, antimony, and tellurium.

[0019] An embodiment method for preparing the compositions involves the use of melt spinning. Melt spinning involves sending a composition in the form of a melt to a spinning wheel. When the melt contacts the spinning wheel, it loses heat and solidifies. A schematic representation showing the production of the compositions by melt spinning is shown in FIG. 1. Melt spinning apparatus 10 includes crucible 12 filled with powder 14 and surrounded by induction heating coils 16. Crucible 12 can be made from a material such as, but not limited to, boron nitride, and may be provided with a coupling (a tantalum coupling, for example) to facilitate the heating process. Melt spinning apparatus 10 also includes melt spinning chamber 18 and spinning wheel 20 (a copper wheel, for example) inside the chamber. During operation, the induction heating coils transfer energy to the crucible (a coupler facilitates this, depending on the choice of crucible materials), and powder 14 inside the crucible heats until it melts. The melt exits the crucible through opening 22 at the bottom of crucible 12 and moves into melt-spinning chamber 18 where it makes contact with spinning wheel 20. The melt cools as it contacts the wheel, and is sent through snout 24 where it is collected as flakes 26. A non-limiting range of speeds of the spinning wheel may be from about 1 rpm to about 5000 rpm, or from about 1000 to about 3000 rpm, or from about 1000 rpm to about 2000 rpm, or from about 1000 rpm to about 1700 rpm. An embodiment composition produced by sending a melt to the spinning wheel may be in the form of flakes that include crystalline nanoparticles in a glassy matrix. The chemical formula for the crystalline nanoparticle portion of the flakes may be essentially the same as that for the glassy matrix.

[0020] Powders may be used as starting materials. A cerium doped lanthanum bromide ( $\text{LaBr}_3\text{:Ce}$ ) embodiment composition, for example, may be prepared from a mixture of cerium bromide ( $\text{CeBr}_3$ ) powder and lanthanum bromide ( $\text{LaBr}_3$ ) powder. A terbium doped lanthanum chloride

(LaCl<sub>3</sub>:Tb) embodiment composition may be prepared from a mixture of terbium chloride (TbCl<sub>3</sub>) powder and lanthanum chloride (LaCl<sub>3</sub>). A samarium doped lanthanum bromide/chloride (LaBr<sub>(3-x)</sub>Cl<sub>x</sub>:Sm) embodiment composition may be prepared from a powder mixture of samarium bromide (SmBr<sub>3</sub>), lanthanum bromide, and lanthanum chloride. A praseodymium doped lanthanum fluoride (LaF<sub>3</sub>:Pr) embodiment composition may be prepared from a mixture of praseodymium fluoride (PrF<sub>3</sub>) and lanthanum fluoride (LaF<sub>3</sub>). Other embodiment compositions include but are not limited to, CeBr<sub>3</sub>, YAlO<sub>3</sub>:Ce, LuAlO<sub>3</sub>:Ce, Lu<sub>1-x</sub>Y<sub>x</sub>O<sub>3</sub>:Ce, Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>, PbWO<sub>4</sub>, CdWO<sub>4</sub>, Lu<sub>2</sub>SiO<sub>5</sub>:Ce, Y<sub>2</sub>SiO<sub>5</sub>:Ce, Lu<sub>2-x</sub>Y<sub>x</sub>SiO<sub>5</sub>:Ce, MgF<sub>2</sub>:Ce, CaF<sub>2</sub>:Ce, BaF<sub>2</sub>:Ce, LaCl<sub>3</sub>:Ce, K<sub>2</sub>LaCl<sub>5</sub>:Ce, LaBr<sub>3</sub>:Ce, RbGd<sub>2</sub>Br<sub>3</sub>:Ce, CsI:Na, CsI, CsI:Ti, NaI:Ti, ZnS:Ag, and the like.

**[0021]** The amount of each powder used in preparing an embodiment composition depends on the desired amounts of dopant and other ingredients in the composition. From the formula of an embodiment composition, the amount of each ingredient can be calculated.

**[0022]** When powders are used, any mixing device or method may be used to mix the powder. Mixing devices should not generate impurities that remain in a product phosphor composition, or generate only a minimal amount that does not substantially affect properties of the composition. Some non-limiting examples of methods and devices for mixing powder include mortar/pestle, ball milling, mixer mixing, attrition milling, and jet milling. Some or all of these methods and devices are employed in industrial operations. A mill containing spherical or rod-like materials, for example, may be used as the mixing device. In such a mill, the inner wall of the mill and the spherical or rod-like materials could be made of highly pure (at least 99.9 percent) alumina in order to avoid, or at least minimize impurities in a composition. The surface of a mixing device that contacts powder precursor could be made of plastic or coated with plastic. Some non-limiting examples of plastics include polyethylene, polypropylene, polyamides, polyesters and polyurethanes. The use of plastic tends to minimize impurities generated during a mixing operation.

**[0023]** After a mixing operation, precursor powder is heated to form a melt. The melting process can enhance the mixing significantly, and therefore an extensive grinding of powder prior to melting may not be necessary, which may avoid or minimize impurities that tend to result from grinding powder. When lanthanum halide precursor powder is used, for example, a non-limiting temperature range for heating a melt may be from about 100° C. to about 2800° C., or from about 800° C. to about 950° C.

**[0024]** The melting of precursor powder can take place in a crucible having a small opening and nozzle. A melt once generated in the crucible can flow through the nozzle. The flow through the opening/nozzle can be enhanced using pressurized gas. Additional mixing action may take place as a melt moves through the opening/nozzle and out of the crucible. This type of mixing action is believed to be similar to that of a vortex, which can enhance the uniformity of the components in the melt. The nozzle opening should be large enough for the melt to flow through, aided with pressure from a jet of inert gas (argon, for example). A non-limiting range of nozzle opening sizes for a crucible may be from about 0.006 to about 0.1 inches, or from about 0.01 to about 0.03 inches, or from about 0.010 inches to about 0.020 inches. Without wishing to be bound by any explanation, it is believed that the

mixing, melting and flow of melt through the nozzle of a crucible is believed to cause mixing of the precursor on an atomic scale.

**[0025]** It should be understood that there is no particular restriction on the size and shape of the crucible. A tube shape with a small opening at the bottom of the crucible, for example, could be used. A crucible with a continuous feeding device could be used.

**[0026]** It is believed that a uniform distribution of components is formed in the melt, and that this uniform distribution does not change when the melt contacts the spinning wheel, loses heat, and solidifies. The cooling provided by the spinning wheel is believed to prevent segregation of a component as particles form after the melt contacts the spinning wheel.

**[0027]** In some embodiments for preparing rare earth doped lanthanum halide compositions, the temperature of the melt and the rate of spinning of a spinning wheel were such that the product phosphor composition produced was in the form of nanoparticles of rare earth doped lanthanum halide embedded in a glassy matrix. In one of these embodiments, flakes of nanoparticles of cerium-doped lanthanum bromide LaBr<sub>3</sub>:Ce embedded in a glassy matrix were prepared by mixing LaBr<sub>3</sub> powder with CeBr<sub>3</sub> powder using a mortar and pestle under argon in a glove box, loading the powder into a boron nitride crucible, transferring the loaded crucible to a melt spinner apparatus, melting the powder and injecting the melt through a nozzle on the crucible to a spinning copper wheel. The molten material was forced through the opening using pressurized gas (argon, for example). By using different pressures of the pressurized gas, the flow of the molten material through the opening in the crucible and therefore the feeding rate of the molten material to the copper spinning wheel can be adjusted.

**[0028]** The viscosity of the molten material can be adjusted by adjusting the temperature of the molten material. The viscosity also has an effect on the flow of molten material through the opening in the crucible. The rotation of the spinning wheel promotes cooling of the copper wheel, which is cool before it is exposed to any new molten material. The molten material is cooled rapidly as it contacts the wheel. As the molten material cools, it forms flakes. In an embodiment, these flakes include nanoparticles of cerium doped lanthanum bromide (i.e. LaBr<sub>3</sub>:Ce) having an average particle of less than about 100 nanometers (nm) embedded in a glassy LaBr<sub>3</sub>:Ce matrix. The LaBr<sub>3</sub>:Ce product produced according to this embodiment has good light output and energy resolution.

**[0029]** In an embodiment, melt spinning of LaBr<sub>3</sub>:Ce results in nanoparticles LaBr<sub>3</sub>:Ce of a uniform size.

**[0030]** In an aspect of the invention related to LaBr<sub>3</sub>:Ce formation, LaBr<sub>3</sub>:Ce nanoparticles having better light output and energy resolution than conventional methods is obtainable because impurities that typically result from an extensive milling step and from hydrate formation can be minimized or completely prevented.

**[0031]** It should be understood that the choice of lanthanides and dopants are not limited to lanthanum (La) and cerium (Ce), and that any lanthanide capable of functioning as an inert host into which an emitting ion may be doped, may be used with the invention. These include La, Ce, Y, Nd, Cd, W, Mg, Ca, Ba, Na, K, Cs. The host can be any halide, oxyhalide, oxide, nitride, oxynitride, carbide, oxycarbide, or boride. The dopant can be Ce, Pr, Tm, Tb, Gd, Dy, Cr, Mn, Ti, Cu, Zn, Ga, Sb, Te, Eu, Sm, Y, Tl, Na, Li, B, Ag, or Nd. The

choice of lanthanide may be tailored in order to prepare a chosen nanophosphor having desired emission properties.

**[0032]** Some embodiment compositions may be prepared from powders. The amount of each powder can be calculated for a desired composition. One example of a powder composition is one with both  $\text{LaBr}_3$  powder and  $\text{CeBr}_3$  powder. Another embodiment powder is one with  $\text{LaBr}_3$ ,  $\text{LaCl}_3$ , and  $\text{CeBr}_3$ . In some of these,  $\text{CeBr}_3$  powder is combined with  $\text{LaBr}_3$  powder in a composition with a mole percent of cerium in a range of from 0.01 mole percent to 20 mole percent. A melt spun product may be one of the formula  $\text{La}_{1-x}\text{Br}_{3-y}\text{Cl}_y\text{Ce}_x$  wherein x is from 0 to 1, and wherein y is from 0 to 3. Both x and y can be fractional numbers. In some embodiments, cerium is not introduced as a bromide but instead it may be introduced as cerium metal, as an organometallic compound of cerium as cerium oxide, as cerium fluoride, as cerium chloride, as cerium nitrate, or in any other form.

**[0033]** In demonstrating the operability of the invention, raw materials were used for preparing some embodiment compositions that included  $\text{LaBr}_3$ ,  $\text{LaCl}_3$ , and  $\text{CeBr}_3$  also included some impurities. The amounts of the impurities were determined using Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS). TABLE 1 below provides a listing of the impurities.

TABLE 1

Impurity	$\text{LaBr}_3$ (ppm)	$\text{LaCl}_3$ (ppm)	$\text{CeBr}_3$ (ppm)
Aluminum	21	—	—
Arsenic	31	—	—
Barium	—	—	—
Boron	—	—	—
Bromine	—	410	—
Cadmium	—	—	—
Calcium	—	77	67
Copper	—	—	—
Gadolinium	—	—	—
Iron	16	—	—
Lanthanum	—	—	21
Magnesium	6	—	—
Manganese	27	—	—
Lithium	—	—	—
Potassium	—	—	—
Sodium	—	—	—
Tellurium	—	—	—
Thorium	6	—	—
Titanium	—	—	—
Uranium	—	—	—
Total	107	487	88

According to TABLE 1,  $\text{CeBr}_3$  has the lowest content of impurities (total of less than 100 ppm). Although  $\text{LaCl}_3$  had a high impurity content, most of the impurity is Br, which is a major component of  $\text{LaBr}_3$  and so can be used to form a melt with  $\text{LaBr}_3$  without contributing to the overall impurity content.

**[0034]** A Differential Scanning Calorimeter (DSC) was used to evaluate reactions between the raw material and crucible materials and to provide guidance on the melt temperature during melt spinning. A small batch of  $\text{LaBr}_3$ ,  $\text{LaCl}_3$ , and  $\text{CeBr}_3$  raw powders yielding a  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{1.575}\text{Cl}_{1.425}$  composition was mixed using high purity aluminum oxide mortar and pestle. Powder mixing was performed in a glove box. The mixture powder was added into four different types of crucibles including  $\text{Al}_2\text{O}_3$ , BN, Pt, and quartz to investigate the possibility of reaction between crucible material and raw materials. The raw material was heated in the crucible to

melting in an Ar environment with a heating rate of  $20^\circ\text{C./min}$ . The results indicate that there is no reaction with any crucible materials including  $\text{Al}_2\text{O}_3$ , BN, Pt, and quartz. These results confirm that  $\text{Al}_2\text{O}_3$ , BN, Pt, and quartz can be used as crucible materials for melt spinning an inorganic composition.

**[0035]** DSC was performed on the as-received  $\text{LaBr}_3$  material (TABLE 1).  $\text{LaBr}_3$  powders were loaded into the BN crucible inside a glove box, and moisture content was maintained at less than 50 ppm. The crucible with  $\text{LaBr}_3$  powder was quickly transferred to the DSC with BN lid protection. The test was performed with a heating rate of  $20^\circ\text{C./min}$  in an Ar environment. FIG. 2 shows typical DSC result from  $\text{LaBr}_3$  powders. As can be seen from FIG. 2, some moisture that adsorbed on the powder surface was removed at about  $91^\circ\text{C}$ . In addition, some crystalline water was removed at about  $372^\circ\text{C}$ . The strong endothermic peak indicates that  $\text{LaBr}_3$  starts to melt at about  $788^\circ\text{C}$ .

**[0036]** DSC was performed on the as-received  $\text{LaCl}_3$  materials.  $\text{LaCl}_3$  powders were loaded into the BN crucible inside a glove box, and moisture content was maintained at less than 50 ppm. The crucible with  $\text{LaCl}_3$  powder was quickly transferred to the DSC with BN lid protection. The test was performed with a heating rate of  $20^\circ\text{C./min}$  in an Ar environment. FIG. 3 shows typical DSC result from  $\text{LaCl}_3$  powders. As can be seen from FIG. 3,  $\text{LaCl}_3$  has a moisture adsorption at  $125^\circ\text{C}$ ., however it does not have the crystalline water at about  $400^\circ\text{C}$ . This is an indication that  $\text{LaCl}_3$  is less sensitive to the moisture than  $\text{LaBr}_3$ . The melting point of  $\text{LaCl}_3$  is at  $877^\circ\text{C}$ .

**[0037]** A small batch of  $\text{LaBr}_3$  and  $\text{CeBr}_3$  raw powders yielding  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$  composition was mixed using high purity aluminum oxide mortar and pestle. The mixture powders were also analyzed using DSC. FIG. 4 shows typical DSC results from  $\text{LaBr}_3$  powders with 5 mole percent of  $\text{CeBr}_3$ . From this figure, one can see that the melting is reduced slightly to about  $785^\circ\text{C}$ . due to the eutectic composition. In addition to the removal of moisture at about  $125$  and  $400^\circ\text{C}$ ., there is additional moisture removal at about  $334^\circ\text{C}$ . Furthermore, the stronger peak at  $334^\circ\text{C}$ . might be an indication that  $\text{CeBr}_3$  is much more sensitive to moisture.

**[0038]** A small batch of  $\text{LaBr}_3$ ,  $\text{LaCl}_3$ , and  $\text{CeBr}_3$  raw powders yielding a  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$  composition was mixed using high purity aluminum oxide mortar and pestle. FIG. 5 shows typical DSC results from  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$  with  $\text{LaBr}_3/\text{LaCl}_3$  of 75/25 mole ratio. This powder composition has 5 mole percent of  $\text{CeBr}_3$ . As indicated in FIG. 5, the melting point of the  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$  mixture is lower because of the ternary eutectic.

**[0039]** A small batch of  $\text{LaBr}_3$ ,  $\text{LaCl}_3$ , and  $\text{CeBr}_3$  raw powders yielding a  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{1.575}\text{Cl}_{1.425}$  composition was mixed using high purity aluminum oxide mortar and pestle. FIG. 6 shows typical DSC results from  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{1.575}\text{Cl}_{1.425}$  with  $\text{LaBr}_3/\text{LaCl}_3$  in a 50/50 mole ratio. This powder composition has 5 mole % of  $\text{CeBr}_3$ . As indicated in FIG. 6, the melting point for the  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{1.575}\text{Cl}_{1.425}$  composition has a higher melting point due to the higher amount of high melting point constituent  $\text{LaCl}_3$ .

**[0040]** The following non-limiting EXAMPLES provide detailed procedures for the preparation of some embodiment inorganic compositions that are also scintillators.

## EXAMPLE 1

**[0041]** Preparation of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$ . A uniform powder mixture of lanthanum bromide ( $\text{LaBr}_3$ , 40 grams) and cerium bromide ( $\text{CeBr}_3$ , 2.11 grams) was prepared using a mortar and pestle in a glove box. The resulting mixture was transferred to a boron nitride crucible. The crucible had a nozzle with an opening of 0.019 inches. The crucible and powder were transferred from the glove box to the induction-heating coil of a melt spinner apparatus. A niobium shield was machined to serve as a coupling from the crucible/powder to the induction coil. The induction coil was water cooled to prevent the coil from overheating. After twice evacuating and purging the system with argon, the induction power was turned on to melt the powder. The peak temperature was set at 870° C. with a heating rate of about 20° C./min. The copper wheel was turned on and the turning speed was increased slowly to about 1000 rpm. After the temperature had stabilized for about 2 minutes, a 3 psi jet of argon was used to inject the molten  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$  through the nozzle opening and onto the copper wheel. As the melt contacted the wheel, it was converted to flakes that sprayed into the snout section the collecting area. A funnel made out of aluminum foil was made as liner for the snout to minimize exposure to moisture. The translucent flakes were collected quickly under argon in a glass container and transferred to a glove box. Yield: about 4 grams. The flakes appear to be agglomerates held loosely together because they break up easily. FIG. 7 shows a TEM micrograph of the flaky product. As can be seen from FIG. 7, the flakes include large numbers of small particles of a size on the order of about 20 nm. According to the diffused rings of the diffraction pattern, the product is a composition of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$  nanoparticles that are embedded in a glassy  $\text{LaBr}_3\text{:Ce}$  matrix.

## EXAMPLE 2

**[0042]** Preparation of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$ . A uniform powder mixture of  $\text{LaBr}_3$  (40 grams),  $\text{LaCl}_3$  (8.64 grams), and  $\text{CeBr}_3$  (2.11 grams) was prepared inside a glove box using a mortar and pestle made of high purity aluminum oxide. The mixture was poured into a boron nitride crucible inside the glove box, and then loaded into an induction-heating coil in a melt spinner apparatus. A tantalum (Ta) shield was machined to serve as a coupling to the induction coil. The induction coil was water cooled to prevent the coil from overheating. The apparatus was evacuated and then purged with argon. After repeating the evacuation/purging process to minimize the presence of oxygen and moisture, the induction power was turned on to heat up the powder. The apparatus peak temperature was set at 870° C. with a heating rate of about 20° C./min. The copper wheel was turned on and the turning speed was increased slowly to about 2000 rpm. After the temperature had stabilized for about 2 minutes, an argon jet of 1 psi was applied to inject the molten  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$  through the nozzle opening and onto the copper wheel. The opening of the BN nozzle was about 0.019". The nozzle was lowered to toward the copper wheel, which reduced the distance between the nozzle and the copper wheel. Due to the small distance between the nozzle and the wheel, all of the melt was splashed randomly instead of going into the snout area. The splashed products were chunky with irregular structure. FIG. 8 shows an X-ray diffraction pattern of the product.

**[0043]** An x-ray diffraction (XRD) spectrum of the nanoparticle composition of EXAMPLE 6 is shown in FIG. 8. The

XRD pattern of  $\text{LaX}_3\text{:Ce}$  shows the expected lines of the tysonite structure, and the absence of other lines indicates high phase purity.

## EXAMPLE 3

**[0044]** Preparation of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$ . A uniform powder mixture of  $\text{LaBr}_3$  (40 g),  $\text{LaCl}_3$  (8.64 g) and  $\text{CeBr}_3$  (2.11 g) was prepared in a glove box using a mortar and pestle. The powder mixture was transferred to a boron nitride crucible. The crucible had a nozzle opening of 0.019 inches. The crucible and powder were transferred to the induction-heating coil of a melt spinner apparatus. A niobium shield was machined to serve as a coupling to the induction coil. The induction coil was water cooled to prevent the coil from overheating. After twice evacuating and purging the system with argon, the induction power was turned on to melt the powder mixture. The peak temperature was set at 870° C. with a heating rate of about 20° C./min. The copper wheel was also turned on and the turning speed was increased slowly to about 1700 rpm. After the temperature had stabilized for about 2 minutes, a 1 psi jet of argon was used to inject the molten  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_3$  through the nozzle opening and onto the copper wheel. As the melt contacted the wheel, it was converted to solid flakes. The flakes were sprayed into the snout section of the collecting area. The flakes were collected quickly under argon in a glass container and transferred to a glove box. Yield: about 10 grams.

## EXAMPLE 4

**[0045]** Preparation of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$ . The procedure of EXAMPLE 3 was followed with the exception that a tantalum shield was used instead of a niobium shield, and the speed of the rotating wheel was about 2000 rpm instead of 1700 rpm. Yield: about 12 grams.

## EXAMPLE 5

**[0046]** Preparation of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$ . The procedure of EXAMPLE 3 was followed with the exception that a tantalum shield was used instead of a niobium shield, the speed of the rotating wheel was about 2000 rpm instead of 1700 rpm, and the nozzle opening of the crucible was 0.010 inches instead of 0.019 inches. The melt-spun flakes were much smaller and had a finer texture than those of EXAMPLE 3 or EXAMPLE 4.

## EXAMPLE 6

**[0047]** Attempted preparation of  $\text{La}_{0.95}\text{Ce}_{0.05}\text{Br}_{2.288}\text{Cl}_{0.713}$  using a crucible with a very small nozzle opening. The procedure of EXAMPLE 4 was repeated with the exception that the nozzle opening was 0.005 inches. At a peak temperature of 870° C. and an argon jet pressure of about 1 psi, no melt could be injected out of the nozzle. When the argon jet pressure was increased to about 12 psi, still no melt could be injected. When the melt temperature was increased to about 1300° C. with an argon jet pressure of 12 psi, still no melt could be injected through the nozzle.

**[0048]** Some embodiment compositions are phosphors that may be used for radiation detection. Large-area radiographic devices are often based on tiled mosaics of single crystals or an array of single crystal pixels. These devices suffer from disadvantages associated with non-uniform light output over the large area of the detector, and from the dark contrast lines that result from the seams between the tiles or pixels. Another

significant problem associated with the production of pixelated detectors relates to the difficulty in producing pixels; some materials, such as the known scintillator  $\text{Gd}_2\text{SiO}_5\text{:Ce}$  (GSO:Ce) single crystals are micaceous and cannot be easily cut into pixels and polished for use in radiographic imaging. By contrast, embodiment compositions of this invention are expected to have a relatively uniform light output, can be made seamless over a large area. They can be used in detectors for proton and neutron radiography, for positron emission tomography, and for medical radiography. Relatively inexpensive, large area detectors (portal monitors, shipping containers, medical imagers, and the like) are possible because the process for making embodiment phosphor compositions can be scaled up to form large amounts of the compositions. The compositions may be used in radiation detectors for interrogation of complex and irregular shapes.

[0049] By selecting the appropriate rare earth dopant, the light emission from the radiation detector can be tailored for either a photomultiplier or a photodiode.

[0050] The EXAMPLES described above involve preparation of a product using a batch type process on a relatively small scale. It should be understood that the process could be scaled up so that much greater amounts of product could be obtained. In addition, the process could be changed from a batch type to a continuous type process. This could be accomplished by using, for example, a continuous feed mechanism such as a screw feed for continuously delivering powder at a controlled rate into the melt crucible. Such a feeder would be used with an airlock system for delivering powder without opening the melt spinner to the atmosphere. A larger crucible with multiple ejection nozzles would be used. The crucible could be heated by induction heating, resistance heating, or by using radiant heat. A wheel large enough to accommodate the multiple ejection nozzles would be used. The wheel would be actively cooled using, for example, water or gas. A continuous or batch removal system that allows product to exit the melt spinner without letting air into it would also be used.

[0051] In summary, inorganic compositions were prepared by sending an inorganic melt to a spinning wheel. Some of the products were shown to be nanostructured, having nanoparticles embedded in a glassy matrix.

[0052] The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching.

[0053] The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

What is claimed is:

1. A process for preparing a composition, comprising:  
sending an inorganic melt to a spinning wheel, whereby the melt cools after it contacts the wheel and is converted into a product that comprises nanoparticles embedded in a glassy matrix.
2. The process of claim 1, wherein the step of sending the inorganic melt to a spinning wheel further comprises sending the inorganic melt through a narrow nozzle.
3. The process of claim 1, wherein the product comprises a scintillator.

4. The process of claim 1, wherein the inorganic melt is sent to the spinning wheel under an inert atmosphere that comprises argon, nitrogen, helium, or mixtures thereof.

5. The process of claim 1, wherein the inorganic melt is sent to the spinning wheel in a continuous process.

6. The process of claim 1, wherein the inorganic melt is sent to the spinning wheel in a batch type process.

7. The process of claim 1, wherein the inorganic melt comprises Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, B, C, N, O, F, Cl, Br, I, At, Al, Si, P, S, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or combinations thereof.

8. The process of claim 1, wherein the inorganic melt comprises an oxide, a nitride, an oxynitride, a sulfide, a phosphide, a selenide, a carbide, an oxycarbide, a boride, a halide, an oxyhalide, an organometallic compound, or combinations thereof.

9. The process of claim 1, further comprising forming an inorganic melt from a powder mixture comprising lanthanum halide and rare earth material.

10. The process of claim 9, wherein the weight ratio of lanthanum halide powder to rare earth material is in a range of from about 10,000:1 to about 1:100.

11. The process of claim 8, wherein the lanthanum halide comprises lanthanum fluoride, lanthanum chloride, lanthanum bromide, lanthanum iodide, or mixtures thereof.

12. The process of claim 1, wherein the solid composition is of the formula  $\text{M}_{1-x}\text{Br}_{3-y}\text{Cl}_y\text{:Q}_x$ , wherein M is a lanthanide or an actinide, wherein x is less than or equal to one, wherein Q is a rare earth element, and wherein y is less than or equal to 3.

13. The process of claim 12, wherein M is chosen from yttrium, lanthanum, gadolinium, lutetium, and combinations thereof.

14. The process of claim 12, wherein Q is chosen from cerium, samarium, europium, terbium, and praseodymium.

15. A product prepared by a process that comprises sending an inorganic melt to a spinning wheel that cools the melt after the melt contacts the spinning wheel, whereby the melt is converted into a product that comprises nanoparticles of a composition embedded in a glassy matrix of essentially the same composition.

16. The product of claim 15, wherein said product comprises a scintillator.

17. The product of claim 15, wherein said product is of the formula  $\text{M}_{1-x}\text{Br}_{3-y}\text{Cl}_y\text{:Q}_x$ , wherein M is a lanthanide or an actinide, wherein x is less than one, wherein Q is a rare earth element, and wherein y is less than or equal to 3.

18. The product of claim 15, wherein M is chosen from yttrium, lanthanum, gadolinium, lutetium, and combinations thereof.

19. The product of claim 17, wherein Q is chosen from cerium, samarium, europium, terbium, and praseodymium.

20. The product of claim 15, wherein the product comprises Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, B, C, N, O, F, Cl, Br, I, At, Al, Si, P, S, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or combinations thereof.

21. The product of claim 15, wherein said product comprises a halide, an oxide, a nitride, an oxynitride, a sulfide, a

phosphide, a selenide, a carbide, an oxycarbide, a boride, a halide, an oxyhalide, an organometallic compound, or combinations thereof.

**22.** The product of claim **15**, wherein said product comprises  $\text{CeBr}_3$ ,  $\text{YAlO}_3\text{:Ce}$ ,  $\text{LuAlO}_3\text{:Ce}$ ,  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ,  $\text{PbWO}_4$ ,  $\text{CdWO}_4$ ,  $\text{Lu}_2\text{SiO}_5\text{:Ce}$ ,  $\text{Y}_2\text{SiO}_5\text{:Ce}$ ,  $\text{MgF}_2\text{:Ce}$ ,  $\text{CaF}_2\text{:Ce}$ ,  $\text{BaF}_2\text{:Ce}$ ,  $\text{LaCl}_3\text{:Ce}$ ,  $\text{K}_2\text{LaCl}_5\text{:Ce}$ ,  $\text{LaBr}_3\text{:Ce}$ ,  $\text{RbGd}_2\text{Br}_3\text{:Ce}$ ,  $\text{CsI:Na}$ ,  $\text{CsI:Tl}$ ,  $\text{NaI:Tl}$ ,  $\text{ZnS:Ag}$ , or combinations thereof.

**23.** The product of claim **15**, wherein said product comprises nanoparticles.

**24.** A composition that consists essentially of nanoparticles of a composition embedded in a glassy matrix of essentially the same composition as that of the nanoparticles.

**25.** The composition of claim **23**, wherein said composition is of the formula  $\text{M}_{1-x}\text{Br}_{3-y}\text{Cl}_y\text{:Q}_x$ , wherein M is a lanthanide or an actinide, wherein x is less than or equal to one, wherein y is less than or equal to 3.

**26.** The composition of claim **23**, wherein M is chosen from yttrium, lanthanum, gadolinium, lutetium, and combinations thereof.

**27.** The composition of claim **23**, wherein Q is chosen from cerium, samarium, europium, terbium, and praseodymium.

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