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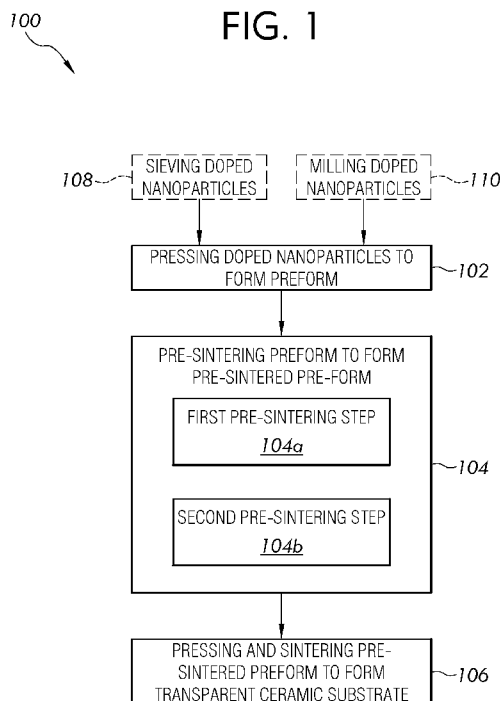
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(57) Abstract: A method of forming a transparent ceramic substrate includes pressing doped nanoparticles to form a preform, pre-sintering the preform, and pressing and sintering the pre-sintered preform to form the transparent ceramic substrate. The pre-sintering includes a first pre-sintering step including heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature greater than or equal to 1450 °C and less than or equal to 1600 °C and a second pre-sintering step including heating the preform at a second furnace temperature greater than or equal to 1350 °C and less than or equal to 1500 °C to form the pre-sintered preform.

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**METHODS OF FORMING TRANSPARENT CERAMIC SUBSTRATES,  
TRANSPARENT CERAMIC SUBSTRATES AND  
QUANTUM MEMORY SYSTEMS**

**Cross-reference to Related Applications**

[0001] This application claims the benefit of priority of U.S. Provisional Application Serial No. 63/604,682, filed on November 30, 2023, the content of which is relied upon and incorporated herein by reference in its entirety.

***Field***

[0002] The present specification generally relates to transparent ceramic substrates and, in particular, to methods of forming transparent ceramic substrates having reduced scattering and improved optical transparency.

***Technical Background***

[0003] Rare earth-doped transparent ceramic single-mode waveguides are desired platforms for optical quantum memories. Such waveguide structures offer advantages such as low insertion loss, simple packaging, and device stability. However, fabrication processes for these ceramic waveguide quantum memories is challenging, as optical scattering due to residual porosity in the resulting ceramic may be a source of optical loss.

[0004] Accordingly, a continual need exists for methods of forming transparent ceramic substrates having reduced scattering and improved optical transparency.

**SUMMARY**

[0005] According to a first aspect A1, a method of forming a transparent ceramic substrate comprises: pressing doped nanoparticles to form a preform; pre-sintering the preform, wherein the pre-sintering comprises: a first pre-sintering step comprising heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature greater than or equal to 1450 °C and less than or equal to 1600 °C; and a second pre-sintering step comprising heating the preform at a second furnace temperature greater than or equal to 1350 °C and less than or equal to 1500 °C to form a pre-sintered preform; and pressing and sintering the pre-sintered preform to form the transparent ceramic substrate.

[0006] A second aspect A2 includes the method of the first aspect A1, wherein the ramping to the first furnace temperature is at a ramp rate greater than or equal to 2 °C/min and less than or equal to 10 °C/min.

[0007] A third aspect A3 includes the method of the first aspect A1 or the second aspect A2, wherein the method further comprises reducing the furnace temperature from the first furnace temperature to the second furnace temperature after the first furnace temperature is reached such that the preform is not held for a time period at the first temperature greater than 10 seconds at the first furnace temperature.

[0008] A fourth aspect A4 includes the method of any one of the first through third aspects A1-A3, wherein the preform is held at the second furnace temperature for a time period greater than or equal to 10 hours and less than or equal to 120 hours.

[0009] A fifth aspect A5 includes the method of the third aspect A3 or the fourth aspect A4, wherein the furnace temperature is reduced from the first furnace temperature to the second furnace temperature at a temperature reduction rate greater than or equal to 8 °C/min and less than or equal to 50 °C/min.

[0010] A sixth aspect A6 includes the method of any one of the first through fifth aspects A1-A5, wherein the doped nanoparticles comprise rare-earth doped nanoparticles.

[0011] A seventh aspect A7 includes the method of the sixth aspect A6, wherein the rare-earth doped nanoparticles comprise yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof.

[0012] An eighth aspect A8 includes the method of any one of the first through seventh aspects A1-A7, wherein the method further comprises, prior to the pressing the doped nanoparticles to form the preform, sieving the doped nanoparticles through a sieve.

[0013] A ninth aspect A9 includes the method of the eighth aspect A8, wherein the sieve comprises a mesh size greater than or equal to 10 µm and less than or equal to 500 µm.

[0014] A tenth aspect A10 includes the method of the eighth aspect A8 or the ninth aspect A9, wherein the sieving comprises passing the doped nanoparticles through a mesh.

[0015] An eleventh aspect A11 includes the method of the tenth aspect A10, wherein the sieve comprises a mesh comprising nylon, acrylic, polyester, polyvinyl chloride, or combinations thereof.

[0016] A twelfth aspect A12 includes the method of any one of the first through seventh aspects A1-A7, wherein the method further comprises, prior to the pressing the doped nanoparticles to form the preform, milling the doped nanoparticles.

[0017] A thirteenth aspect A13 includes the method of the twelfth aspect A12, wherein the milling the doped nanoparticles comprises vibrational milling using milling media.

[0018] A fourteenth aspect A14 includes the method of the thirteenth aspect A13, wherein the milling media comprises yttria stabilized milling media, aluminum oxide milling media, or combinations thereof.

[0019] A fifteenth aspect A15 includes the method of any one of the first through fourteenth aspects A1-A14, wherein the pressing and sintering the pre-sintered preform comprises hot iso-statically pressing the pre-sintered preform.

[0020] A sixteenth aspect A16 includes the method of any one of the first through fifteenth aspects A1-A15, wherein the pressing the doped nanoparticles comprises uni-axially pressing the doped nanoparticles.

[0021] A seventeenth aspect A17 includes the method of any one of the first through sixteenth aspects A1-A16, wherein the pressing the doped nanoparticles comprises cold iso-statically pressing the doped nanoparticles.

[0022] An eighteenth aspect A18 includes the method of any one of the first through seventeenth aspects A1-A17, wherein the doped nanoparticles are formed by: mixing a matrix material, a plurality of rare-earth metal dopants, an organic precursor, and water to form a precursor mixture; and heating the precursor mixture to a heating temperature to induce thermal decomposition of the organic precursor and generate a chemical reaction between the matrix material and the plurality of rare-earth metal dopants to form the doped nanoparticles.

[0023] A nineteenth aspect A19 includes the method of any one of the first through seventeenth aspect A1-A17, wherein the doped nanoparticles are formed by: mixing a matrix material, a plurality of rare-earth metal dopants, and water to form a metal salt solution; heating the metal salt solution to form a heated metal salt solution; and mixing the heated metal salt solution with an organic precursor to form the doped nanoparticles.

[0024] A twentieth aspect A20 includes a transparent ceramic substrate made by the method of any one of the first through nineteenth aspects A1-A19, wherein the transparent ceramic substrate has a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.

[0025] A twenty-first aspect A21 includes the transparent ceramic substrate of the twentieth aspect A20, wherein the transparent ceramic substrate has a total transmittance greater than or equal to 72%, as measured at 500 nm.

[0026] A twenty-second aspect A22 includes the transparent ceramic substrate of the twentieth aspect A20 or the twenty-first aspect A21, wherein the transparent ceramic substrate has a relative density greater than or equal to 99%.

[0027] A twenty-third aspect A23 includes the transparent ceramic substrate of any of the twentieth through twenty-second aspects A20-A22, wherein the transparent ceramic substrate has an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ .

[0028] A twenty-fourth aspect A24 includes the transparent ceramic substrate of any of the twentieth through twenty-third aspects A20-A23, wherein the transparent ceramic substrate has a thickness greater than or equal to 1 mm and less than or equal to 20 mm.

[0029] A twenty-fifth aspect A25 includes the transparent ceramic substrate of any of the twentieth through twenty-fourth aspects, A20-A24, wherein the transparent ceramic substrate is a doped ceramic optical device.

[0030] A twenty-sixth aspect A26 includes a quantum memory system comprising the doped optical device of the twenty-fifth aspect A25.

[0031] According to a twenty-seventh aspect A27, a method of forming a transparent ceramic substrate comprises: subjecting doped nanoparticles to sieving through a sieve or milling; pressing the doped nanoparticles to form a preform; pre-sintering the preform to form a pre-sintered preform; and pressing and sintering the pre-sintered preform to form the transparent ceramic substrate.

[0032] A twenty-eighth aspect A28 includes the method of the twenty-seventh aspect A27, wherein the sieve comprises a mesh size greater than or equal to 10  $\mu\text{m}$  and less than or equal to 500  $\mu\text{m}$ .

[0033] A twenty-ninth aspect A29 includes the method of the twenty-seventh aspect A27 or the twenty-eighth aspect A28, wherein the sieving comprises passing the doped nanoparticles through a mesh.

[0034] A thirtieth aspect A30 includes the method of the twenty-ninth aspect A29, wherein the sieve comprises a mesh comprising nylon, acrylic, polyester, polyvinyl chloride, or combinations thereof.

[0035] A thirty-first aspect A31 includes the method of the twenty-seventh aspect A27, wherein the milling the doped nanoparticles comprises vibrational milling using milling media.

[0036] A thirty-second aspect A32 includes the method of the thirty-first aspect A31, wherein the milling media comprises yttria stabilized milling media, aluminum oxide milling media, or combinations thereof.

[0037] A thirty-third aspect A33 includes the method of any one of the twenty-seventh through thirty-second aspects A27-A32, wherein the doped nanoparticles comprise rare-earth doped nanoparticles.

[0038] A thirty-fourth aspect A34 includes the method of the thirty-third aspect A33, wherein the rare-earth doped nanoparticles comprise yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof.

[0039] A thirty-fifth aspect A35 includes the method of any one of the twenty-seventh through thirty-fourth aspects A27-A34, wherein the pre-sintering comprises a single pre-sintering step, the single pre-sintering step comprising: heating the preform in a furnace by ramping a furnace temperature to a pre-sintering furnace temperature greater than or equal to 1450 °C and less than or equal to 1650 °C; and holding the preform at the pre-sintering furnace temperature for a time period greater than or equal to 1 hour and less than or equal to 10 hours.

[0040] A thirty-sixth aspect A36 includes the method of any one of the twenty-seventh through thirty-fourth aspects A27-A34, wherein the pre-sintering comprises: a first pre-sintering step comprising heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature greater than or equal to 1450 °C and less than or equal to 1600 °C; and a second pre-sintering step comprising heating the preform at a second furnace temperature greater than or equal to 1350 °C and less than or equal to 1500 °C to form a pre-sintered preform.

[0041] A thirty-seventh aspect A37 includes the method of the thirty-sixth aspect A36, wherein the ramping to the first furnace temperature is at a ramp rate greater than or equal to 2 °C/min and less than or equal to 10 °C/min.

[0042] A thirty-eighth aspect A38 includes the method of the thirty-sixth aspect A36 or the thirty-seventh aspect A37, wherein the method further comprises reducing the furnace temperature from the first furnace temperature to the second furnace temperature after the first furnace

temperature is reached such that the preform is not held for a time period at the first temperature greater than 10 seconds at the first furnace temperature.

[0043] A thirty-ninth aspect A39 includes the method of any one of the thirty-sixth through thirty-eighth aspects A36-A38, wherein the preform is held at the second furnace temperature for a time period greater than or equal to 10 hours and less than or equal to 120 hours.

[0044] A fortieth aspect A40 includes the method of the thirty-eighth aspect A38 or the thirty-ninth aspect A39, wherein the furnace temperature is reduced from the first furnace temperature to the second furnace temperature at a temperature reduction rate greater than or equal to 8 °C/min and less than or equal to 50 °C/min.

[0045] A forty-first aspect A41 includes the method of any one of the twenty-seventh through fortieth aspects A27-A40, wherein the pressing and sintering the pre-sintered preform comprises hot iso-statically pressing the pre-sintered preform.

[0046] A forty-second aspect A42 includes the method of any one of the twenty-seventh through forty-first aspects A27-A41, wherein the pressing the doped nanoparticles comprises uni-axially pressing the doped nanoparticles.

[0047] A forty-third aspect A43 includes the method of any one of the twenty-seventh through forty-second aspects A27-A42, wherein the pressing the doped nanoparticles comprises cold iso-statically pressing the doped nanoparticles.

[0048] A forty-fourth aspect A44 includes the method of any one of the twenty-seventh through forty-third aspects A27-A43, wherein the doped nanoparticles are formed by: mixing a matrix material, a plurality of rare-earth metal dopants, an organic precursor, and water to form a precursor mixture; and heating the precursor mixture to a heating temperature to induce thermal decomposition of the organic precursor and generate a chemical reaction between the matrix material and the plurality of rare-earth metal dopants to form the doped nanoparticles.

[0049] A forty-fifth aspect A45 includes the method of any one of the twenty-seventh through forty-third aspects A27-A43, wherein the doped nanoparticles are formed by: mixing a matrix material, a plurality of rare-earth metal dopants, and water to form a metal salt solution; heating the metal salt solution to form a heated metal salt solution; and mixing the heated metal salt solution with an organic precursor to form the doped nanoparticles.

[0050] A forty-sixth aspect A46 includes a transparent ceramic substrate made by the method of any one of the twenty-seventh through forty-fifth aspects A27-A45, wherein the transparent

ceramic substrate has a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.

[0051] A forty-seventh aspects A47 includes the transparent ceramic substrate of the forty-sixth aspect A46, wherein the transparent ceramic substrate has a total transmittance greater than or equal to 72%, as measured at 500 nm.

[0052] A forty-eighth aspect A48 includes the transparent ceramic substrate of the forty-sixth aspect A46 or the forty-seventh aspect A47, wherein the transparent ceramic substrate has a relative density greater than or equal to 99%.

[0053] A forty-ninth aspect A49 includes the transparent ceramic substrate of any one of the forty-sixth through forty-eighth aspects A46-A48, wherein the transparent ceramic substrate has an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ .

[0054] A fiftieth aspect A50 includes the transparent ceramic susbtrate of any one of the forty-sixth through forty-ninth aspects A46-A49, wherein the transparent ceramic substrate has a thickness greater than or equal to 1 mm and less than or equal to 20 mm.

[0055] A fifty-first aspect A51 includes the transparent ceramic susbtrate of any one of the forty-sixth through fiftieth aspects A46-A50, wherein the transparent ceramic substrate is a doped ceramic optical device.

[0056] A fifty-second aspects A52 includes a quantum memory system comprising the doped ceramic optical device of the fifty-first aspect A51.

[0057] According to a fifty-third aspect A53, a quantum memory system comprises: a doped ceramic optical device, the doped ceramic optical device comprising: yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof; and a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.

[0058] A fifty-fourth aspect A54 includes the quantum memory system of the fifty-third aspect A53, wherein the doped ceramic optical device has a total transmittance greater than or equal to 72%, as measured at 500 nm.

[0059] A fifty-fifth aspect A55 includes the quantum memory system of the fifty-third aspect A53 or the fifty-fourth aspect A54, wherein the doped ceramic optical device has a relative density greater than or equal to 99%.

[0060] A fifty-sixth aspect A56 includes the quantum memory system of any one of the fifty-third through fifty-fifth aspects A53-A55, wherein the doped ceramic optical device has an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ .

[0061] A fifty-seventh aspect A57 includes the quantum memory system of any one of the fifty-third through fifty-sixth aspects A53-A56, wherein the doped ceramic optical device has a thickness greater than or equal to 1 mm and less than or equal to 20 mm.

[0062] Additional features and advantages of the transparent ceramic substrates and methods of forming same described herein will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0063] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0064] FIG. 1 is a flow chart of a method of forming a transparent ceramic substrate, according to one or more embodiments described herein;

[0065] FIG. 2A is a schematic illustration of a precursor mixture used to form doped nanoparticles, according to one or more embodiments described herein;

[0066] FIG. 2B is a magnified schematic illustration of the precursor mixture of FIG. 2A;

[0067] FIG. 3A is a schematic illustration of a plurality of doped nanoparticles, according to one or more embodiments described herein;

[0068] FIG. 3B is a magnified schematic illustration of the plurality of doped nanoparticles of FIG. 3A;

[0069] FIG. 4A is a schematic illustration of a metal salt mixture used to form doped nanoparticles, according to one or more embodiments described herein;

- [0070] FIG. 4B is a magnified schematic illustration of the metal salt mixture of FIG. 4A;
- [0071] FIG. 5A is a schematic illustration of the addition of organic precursor to a heated metal salt mixture used to form doped nanoparticles, according to one or more embodiments described herein;
- [0072] FIG. 5B is a magnified schematic illustration of the organic precursor of FIG. 5A;
- [0073] FIG. 5C is a magnified schematic illustration of the heated metal salt mixture of FIG. 5A;
- [0074] FIG. 6A is a schematic illustration of a plurality of doped nanoparticles, according to one or more embodiments described herein;
- [0075] FIG. 6B is a magnified schematic illustration of the plurality of doped nanoparticle of FIG. 6A;
- [0076] FIG. 7A is a plot of temperature (y-axis) versus time (x-axis) of a pre-sintering cycle used to form a pre-sintered preform, according to one or more embodiments described herein;
- [0077] FIG. 7B is a magnified portion of the plot of FIG. 7A;
- [0078] FIG. 8 is a flow chart of another method of forming a transparent ceramic substrate, according to one or more embodiments described herein;
- [0079] FIG. 9 is a schematic illustration of a quantum memory system having a doped ceramic optical device, according to one or more embodiments described herein;
- [0080] FIG. 10 is a schematic illustration of ground and excited energy states, according to one or more embodiments described herein;
- [0081] FIG. 11A is a plot of temperature (y-axis; in °C) versus time (x-axis; in min.) of a pre-sintering cycle used to form an exemplary ceramic pellet, according to one or more embodiments described herein;
- [0082] FIG. 11B is a magnified portion of the plot of FIG. 11A;
- [0083] FIG. 12 is a scanning electron microscope image of a comparative ceramic pellet;
- [0084] FIG. 13 is a grain size distribution of the comparative ceramic pellet shown in FIG. 11;
- [0085] FIG. 14 is a SEM image of a comparative ceramic pellet;
- [0086] FIG. 15 is a grain size distribution of the comparative ceramic pellet shown in FIG. 14;
- [0087] FIG. 16 is a SEM image of a comparative ceramic pellet;
- [0088] FIG. 17 is a grain size distribution of the comparative ceramic pellet shown in FIG. 16;
- [0089] FIG. 18 is a SEM image of a comparative ceramic pellet;

- [0090] FIG. 19 is a grain size distribution of the comparative ceramic pellet shown in FIG. 18;
- [0091] FIG. 20 is a SEM image of a comparative ceramic pellet;
- [0092] FIG. 21 is a grain size distribution of the comparative ceramic pellet shown in FIG. 20;
- [0093] FIG. 22 is a SEM image of a comparative ceramic pellet;
- [0094] FIG. 23 is a grain size distribution of the comparative ceramic pellet shown in FIG. 22;
- [0095] FIG. 24 is a SEM image of an exemplary ceramic pellet, according to one or more embodiments described herein;
- [0096] FIG. 25 is a grain size distribution of the exemplary ceramic pellet shown in FIG. 24;
- [0097] FIG. 26 is a SEM image of an exemplary ceramic pellet, according to one or more embodiments described herein;
- [0098] FIG. 27 is a grain size distribution of the exemplary ceramic pellet shown in FIG. 26;
- [0099] FIG. 28 is a plot of average grain size (y-axis; in microns ( $\mu\text{m}$ )) versus relative density (x-axis; in percentage (%)) of comparative and exemplary ceramic pellets, according to one or more embodiments described herein;
- [00100] FIG. 29 is a plot of average grain size (y-axis; in microns ( $\mu\text{m}$ ) versus  $\text{Ln}(1-D)$  (x-axis;  $D$  is relative density) of comparative and exemplary ceramic pellets, according to one or more embodiments described herein;
- [00101] FIG. 30 is a SEM image of as-synthesized  $\text{Y}_2\text{O}_3$  nanoparticles;
- [00102] FIG. 31 is a SEM image of  $\text{Y}_2\text{O}_3$  nanoparticles after being subjected to sieving, according to one or more embodiments described herein;
- [00103] FIG. 32 is a SEM image of  $\text{Y}_2\text{O}_3$  nanoparticles after being subjected to sieving, according to one or more embodiments described herein;
- [00104] FIG. 33 is a plot of the amount of nanoparticles (y-axis; in percentage (%)) versus the particle size (x-axis; in microns ( $\mu\text{m}$ )) of as-synthesized nanoparticles and sieved nanoparticles, according to one or more embodiments described herein;
- [00105] FIG. 34 are photographs of nanoparticles subjected to milling, according to one or more embodiments described herein;
- [00106] FIG. 35 is a plot of transmitted scatter coefficient (y-axis; in dB/mm) versus wavelength (x-axis; in nanometers (nm)) of a comparative ceramic pellet and example ceramic pellets, according to one or more embodiments described herein; and

[00107] FIG. 36 is a graph of transmitted scatter coefficient (in dB/mm) of a comparative ceramic pellet and example ceramic pellets, according to one or more embodiments described herein.

### DETAILED DESCRIPTION

[00108] Reference will now be made in detail to various embodiments of methods of forming transparent ceramic substrates having reduced scattering and improved optical transparency. According to some embodiments, a method of forming a transparent ceramic substrate includes pressing doped nanoparticles to form a preform, pre-sintering the preform, and pressing and sintering the pre-sintered preform to form the transparent ceramic substrate. The pre-sintering includes a first pre-sintering step including heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature greater than or equal to 1450 °C and less than or equal to 1600 °C and a second pre-sintering step including heating the preform at a second furnace temperature greater than or equal to 1350 °C and less than or equal to 1500 °C to form the pre-sintered preform.

[00109] According to other embodiments, a method of forming a transparent ceramic substrate includes subjecting doped nanoparticles to sieving through a sieve or milling, pressing the doped nanoparticles to form a preform, pre-sintering the preform to form a pre-sintered preform, and pressing and sintering the pre-sintered preform to form the transparent ceramic substrate.

[00110] According to some embodiments, a quantum memory system includes a doped ceramic optical device. The doped ceramic optical device includes yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof. The doped ceramic optical device also has a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.

[00111] Various embodiments of transparent ceramic substrates and methods of forming same will be described herein with specific reference to the appended drawings.

[00112] Ranges may be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[00113] Directional terms as used herein - for example up, down, right, left, front, back, top, bottom - are made only with reference to the figures as drawn and are not intended to imply absolute orientation.

[00114] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order, nor that with any apparatus specific orientations be required. Accordingly, where a method claim does not actually recite an order to be followed by its steps, or that any apparatus claim does not actually recite an order or orientation to individual components, or it is not otherwise specifically stated in the claims or description that the steps are to be limited to a specific order, or that a specific order or orientation to components of an apparatus is not recited, it is in no way intended that an order or orientation be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps, operational flow, order of components, or orientation of components; plain meaning derived from grammatical organization or punctuation, and; the number or type of embodiments described in the specification.

[00115] As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a” component includes aspects having two or more such components, unless the context clearly indicates otherwise.

[00116] “Reduced scattering,” as used herein, refers to a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.

[00117] “Transmitted scatter coefficient,” as used herein, is measured using a Perkin-Elmer 950 spectrophotometer with a 150 mm integration sphere and a measurement range from 250 nm to 2400 nm. Total transmittance ( $T_t$ ) of a sample is measured with a sample attached to an entrance of the integration sphere. Axial transmittance ( $T_a$ ) is measured by placing the sample close to the light source. The transmitted scatter coefficient (SC) is measured according to the following formula:  $SC = 10 \times \log(T_t/T_a)/\text{thickness}$ .

[00118] “Improved optical transparency,” as used herein, refers to a total transmittance greater than or equal to 72%, as measured at 500 nm according. The total transmittance is measured using a Perkin-Elmer 950 spectrophotometer as described herein with respect to “transmitted scatter coefficient.”

[00119] “Density” or “relative density,” as used herein, refers to the ratio of the weight of a material to the apparent loss of weight of the material when immersed in water, as measured according to Archimedes’ density.

[00120] “Grain size,” as used herein, refers to an average of the shortest radius and the longest radius of the grain.

[00121] “Average grain size,” as used herein, refers to an average grain size of a ceramic substrate, as measured using scanning electron microscopy (SEM) according to Mendelson, Mel I. “Average grain size in polycrystalline ceramics.” *Journal of the American Ceramic Society* 52, no. 8 (1969): 443-446.

[00122] “Grain size distribution,” as used herein, refers to grain sizes of a ceramic substrate, as measured using an SEM image including at least 250 grains.

[00123] “Particle size distribution,” as used herein, is measured using a Microtrac S3500, which is a Laser Diffraction (LD) analyzer. Particle size distributions is calculated by the Weibull distribution function, as shown below:

$$F = P_1 \left( 1 - e^{-\left(\frac{x}{\alpha_1}\right)^{\beta_1}} \right) + P_2 \left( 1 - e^{-\left(\frac{x}{\alpha_2}\right)^{\beta_2}} \right) + P_3 \left( 1 - e^{-\left(\frac{x}{\alpha_3}\right)^{\beta_3}} \right) + P_4 \left( 1 - e^{-\left(\frac{x}{\alpha_4}\right)^{\beta_4}} \right) + P_5 \left( 1 - e^{-\left(\frac{x}{\alpha_5}\right)^{\beta_5}} \right)$$

where  $P$  is the percentage of the type of particle,  $\alpha$  the scaling factor, and  $\beta$  is the shape factor that controls distribution shape/peak shape.

[00124] In optical quantum information processing, quantum memory devices enable reversible storage of photons on atoms, and synchronize quantum processing networks. Currently available single-crystals and ceramics have been investigated as quantum memory materials, and specifically rare earth-doped solids, due to narrow 4f-4f transitions of the rare earth ions and a long optical coherence lifetime, on the order of tens of microseconds.

[00125] Transparent ceramics are optically similar to a single crystal and may achieve better optical uniformity (i.e., uniform transmitted scatter coefficient and/or optical transparency throughout). Ceramics may also offer other advantages, such as scalability, relatively low-cost production, and ease of processing. However, optical scattering due to residual porosity in the resulting ceramic may be a source of optical loss.

[00126] Disclosed herein are methods of forming transparent ceramic substrates which mitigate the aforementioned problems. Specifically, the methods of forming transparent ceramic substrates

disclosed herein reduce porosity by increasing density, which results in transparent ceramic substrates having reduced scattering and improved optical transparency. Density may be increased via the two-step pre-sintering described herein, which reduces grain growth while maintaining grain boundary diffusion. Density may additionally or alternatively be increased by reducing the size of the agglomerates of nanoparticles as described herein, which improves packing of the nanoparticles.

**[00127]** Referring now to FIG. 1, a method of forming a transparent ceramic substrate is shown at 100. The method 100 begins at block 102 with pressing doped nanoparticles to form a preform.

**[00128]** In embodiments, the doped nanoparticles may have an average diameter greater than or equal to 20 nm and less than or equal to 400 nm, greater than or equal to 20 nm and less than or equal to 300 nm, greater than or equal to 20 nm and less than or equal to 200 nm, greater than or equal to 20 nm and less than or equal to 100 nm, greater than or equal to 20 nm and less than or equal to 50 nm, greater than or equal to 50 nm and less than or equal to 400 nm, greater than or equal to 50 nm and less than or equal to 300 nm, greater than or equal to 50 nm and less than or equal to 200 nm, greater than or equal to 50 nm and less than or equal to 100 nm, greater than or equal to 100 nm and less than or equal to 400 nm, greater than or equal to 100 nm and less than or equal to 300 nm, greater than or equal to 100 nm and less than or equal to 200 nm, greater than or equal to 200 nm and less than or equal to 400 nm, greater than or equal to 200 nm and less than or equal to 300 nm, or even greater than or equal to 300 nm and less than or equal to 400 nm, or any and all sub-ranges formed from any of these endpoints.

**[00129]** In embodiments, the doped nanoparticles may comprise rare-earth doped nanoparticles. For example, in embodiments, the rare-earth doped nanoparticles may comprise yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof.

**[00130]** Referring now to FIGS. 2A, 2B, 3A, and 3B, in embodiments, the doped nanoparticles may be formed by mixing a matrix material 202, rare-earth metal dopants 204, an organic precursor 206, and water (e.g., deionized water), to form a precursor mixture 208. The matrix material 202 may comprise metal complexes, such as metal salts, which include a rare-earth element, such as yttrium, lanthanum, scandium, lutetium, gadolinium, or combinations thereof, and/or a transition metal, such as zirconium, hafnium, or combinations thereof. In embodiments, the matrix material 202 such as, by way of example,  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ .

[00131] In embodiments, the plurality of rare-earth metal dopants 204 may comprise metal complexes, such as metal salts, that include a rare-earth element, such as erbium, praseodymium, neodymium, samarium, europium, thulium, ytterbium, or combinations thereof. As one example, the rare-earth metal dopants 204 may comprise  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ . By using rare-earth metal dopants 204 to form the doped nanoparticles, the rare-earth dopant may be more uniformly distributed within a crystal lattice of the resultant transparent ceramic substrate, which may be desirable in certain applications, such as to improve the performance of a doped ceramic optical device as described herein.

[00132] In embodiments, the organic precursor 206 may comprise urea, ammonium, hydroxide, or combinations thereof.

[00133] By way of non-limiting examples, the amount of the matrix material 202 in the precursor mixture 208 may be greater than or equal to 40 g and less than or equal to 80 g, greater than or equal to 40 g and less than or equal to 70 g, greater than or equal to 40 g and less than or equal to 60 g, greater than or equal to 50 g and less than or equal to 80 g, greater than or equal to 50 g and less than or equal to 70 g, or even greater than or equal to 50 g and less than or equal to 60 g, or any and all sub-ranges formed from any of these endpoints. The amount of the rare-earth dopants 204 in the precursor mixture 208 may be greater than or equal to 0.01 g and less than or equal to 0.5 g, greater than or equal to 0.01 g and less than or equal to 0.45 g, greater than or equal to 0.01 g and less than or equal to 0.4 g, greater than or equal to 0.01 g and less than or equal to 0.35 g, greater than or equal to 0.01 g and less than or equal to 0.3 g, greater than or equal to 0.05 g and less than or equal to 0.5 g, greater than or equal to 0.05 g and less than or equal to 0.45 g, greater than or equal to 0.05 g and less than or equal to 0.4 g, greater than or equal to 0.05 g and less than or equal to 0.35 g, greater than or equal to 0.05 g and less than or equal to 0.3 g, greater than or equal to 0.1 g and less than or equal to 0.5 g, greater than or equal to 0.1 g and less than or equal to 0.45 g, greater than or equal to 0.1 g and less than or equal to 0.4 g, greater than or equal to 0.1 g and less than or equal to 0.35 g, greater than or equal to 0.1 g and less than or equal to 0.3 g, greater than or equal to 0.15 g and less than or equal to 0.5 g, greater than or equal to 0.15 g and less than or equal to 0.45 g, greater than or equal to 0.15 g and less than or equal to 0.4 g, greater than or equal to 0.15 g and less than or equal to 0.35 g, greater than or equal to 0.15 g and less than or equal to 0.3 g, greater than or equal to 0.2 g and less than or equal to 0.5 g, greater than or equal to 0.2 g and less than or equal to 0.45 g, greater than or equal to 0.2 g and less than or equal to 0.4

g, greater than or equal to 0.2 g and less than or equal to 0.35 g, greater than or equal to 0.2 g and less than or equal to 0.3 g, greater than or equal to 0.25 g and less than or equal to 0.5 g, greater than or equal to 0.25 g and less than or equal to 0.45 g, greater than or equal to 0.25 g and less than or equal to 0.4 g, greater than or equal to 0.25 g and less than or equal to 0.35 g, or even greater than or equal to 0.25 g and less than or equal to 0.3 g, or any and all sub-ranges formed from any of these endpoints. The amount of the organic precursor 206 in the precursor mixture 208 may be greater than or equal to 350 g and less than or equal to 450 g, greater than or equal to 350 g and less than or equal to 425 g, greater than or equal to 350 g and less than or equal to 400 g, greater than or equal to 375 g and less than or equal to 450 g, greater than or equal to 375 g and less than or equal to 425 g, or even greater than or equal to 375 g and less than or equal to 400 g, or any and all sub-ranges formed from any of these endpoints. The amount of water in the precursor mixture 208 may be greater than or equal to 2 L and less than or equal to 6 L, greater than or equal to 2 L and less than or equal to 5 L, greater than or equal to 3 L and less than or equal to 6 L, greater than or equal to 3 L and less than or equal to 5 L, greater than or equal to 4 L and less than or equal to 6 L, or even greater than or equal to 4 L and less than or equal to 5 L, or any and all sub-ranges formed from any of these endpoints.

**[00134]** Referring still to FIGS. 2A, 2B, 3A, and 3B, the precursor mixture 208 including the matrix material 202, the plurality of rare-earth metal dopants 204, the organic precursor 206, and the water may be heated to a heating temperature for a heating period to induce thermal decomposition of the organic precursor 206 and generate a chemical reaction between the matrix material 202 and the rare-earth metal dopants 204 to produce a plurality of rare-earth doped nanoparticles 210, as depicted in FIGS. 3A and 3B. In embodiments, the heating temperature may be greater than or equal to 70 °C and less than or equal to 100 °C, greater than or equal to 80 °C and less than or equal to 100 °C, or even greater than or equal to 90 °C and less than or equal to 100 °C, or any and all sub-ranges formed from any of these endpoints. In embodiments, the heating period may be greater than or equal to 0.5 hour and less than or equal to 3 hours, greater than or equal to 0.5 hour and less than or equal to 2 hours, greater than or equal to 1 hour and less than or equal to 3 hours, or even greater than or equal to 1 hour and less than or equal to 2 hours, or any and all sub-ranges formed from any of these endpoints.

**[00135]** Referring now to FIGS. 4A, 4B, 5A, 5B, 5C, 6A, and 6B, in other embodiments, the doped nanoparticles may be formed by mixing the plurality of matrix material 202, the plurality

of rare-earth metal dopants 204, and deionized water to form a metal salt solution 214. The metal salt solution 214 may include the same or similar amounts of the matrix material 202, the plurality of rare-earth metal dopants 204 and deionized water as the precursor mixture 208 as described hereinabove with respect to FIGS. 2A, 2B, 3A, and 3B.

**[00136]** Referring still to FIGS. 4A, 4B, 5A, 5B, 5C, 6A, and 6B, the metal salt solution 214 may be heated to form a heated metal salt solution 214'. In embodiments, the metal salt solution 214 may be heated to a temperature greater than or equal to 70 °C and less than or equal to 100 °C, greater than or equal to 80 °C and less than or equal to 100 °C, or even greater than or equal to 90 °C and less than or equal to 100 °C, or any and all sub-ranges formed from any of these endpoints. Next, as depicted in FIG. 5A, the organic precursor 206 may be mixed with the heated metal salt solution 214', inducing formation of the rare-earth doped nanoparticles 210. In embodiments, the temperature of the organic precursor 206 may be less than the temperature of the heated metal salt solution 214' when mixed with the heated metal salt solution 214', and in other embodiments, the organic precursor 206 may be the same temperature or a greater temperature than the heated metal salt solution 214'.

**[00137]** In embodiments, forming the heated metal salt solution 214' and then mixing the organic precursor 206 with the heated metal salt solution 214' may induce formation of rare-earth doped nanoparticles 210 that have a smaller diameter than rare-earth doped nanoparticle 210 formed using the precursor mixture 208 as described hereinabove with respect to FIGS. 2A, 2B, 3A, and 3B. For example, the rare-earth doped nanoparticles 210 formed by mixing the organic precursor 206 and the heated metal salt solution 214' may have an average diameter less than or equal to 200 nm, less than or equal to 100 nm, less than or equal to 50 nm, less than or equal to 40 nm, or even less than or equal to 30 nm. While not intending to be limited by theory, it is believed that mixing the organic precursor 206 and the heated metal salt solution 214' produces more rare-earth doped nuclei, thereby forming relatively smaller rare-earth doped nanoparticles 210.

**[00138]** In both the precursor mixture 208 and the heated metal salt solution 214', the thermal decomposition of the organic precursor 206, such as urea, may produce  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ , which react with the transition metals of the matrix material 202 and the rare-earth metals of the plurality of rare-earth metal dopants 204 to produce the plurality of rare-earth doped nanoparticles 210, for example,  $\text{Y}_{1-x}\text{Er}_x(\text{OH})\text{CO}_3 \cdot \text{H}_2\text{O}$  nanoparticles. In embodiments, the  $\text{Y}_{1-x}\text{Er}_x(\text{OH})\text{CO}_3 \cdot \text{H}_2\text{O}$  nanoparticles may be filtered, collected, and annealed at annealing temperature to convert  $\text{Y}_{1-x}$

$x\text{Er}_x(\text{OH})\text{CO}_3 \cdot \text{H}_2\text{O}$  nanoparticles to  $(\text{Y}_{1-x}\text{Er}_x)_2\text{O}_3$  nanoparticles. In embodiments, the annealing temperature may be greater than or equal to 500 °C and less than or equal to 900 °C, greater than or equal to 500 °C and less than or equal to 800 °C, greater than or equal to 500 °C and less than or equal to 700 °C, greater than or equal to 600 °C and less than or equal to 900 °C, greater than or equal to 600 °C and less than or equal to 800 °C, or even greater than or equal to 600 °C and less than or equal to 700 °C, or any and all sub-ranges formed from any of these endpoints. Once annealed, the rare-earth doped nanoparticles 210 may comprise a crystalline structure. In embodiments, the chemical yield of the rare-earth doped nanoparticles 210 may be greater than or equal to 85% and less than or equal to 98%, greater than or equal to 85% and less than or equal to 95%, greater than or equal to 88% and less than or equal to 98%, greater than or equal to 88% and less than or equal to 95%, greater than or equal to 90% and less than or equal to 98%, greater than or equal to 90% and less than or equal to 95%, greater than or equal to 92% and less than or equal to 98%, or even greater than or equal to 92% and less than or equal to 95%, or any and all sub-ranges formed from any of these endpoints.

**[00139]** In embodiments the pressing the doped nanoparticles may comprise uni-axially pressing (i.e., dry pressing) and/or cold iso-statically pressing the doped nanoparticles. The doped nanoparticles may be uni-axially pressed at a pressure greater than or equal to 30 MPa and less than or equal to 50 MPa, greater than or equal to 30 MPa and less than or equal to 45 MPa, greater than or equal to 30 MPa and less than or equal to 40 MPa, greater than or equal to 35 MPa and less than or equal to 50 MPa, greater than or equal to 35 MPa and less than or equal to 45 MPa, or even greater than or equal to 35 MPa and less than or equal to 40 MPa, or any and all sub-ranges formed from any of these endpoints. The doped nanoparticles may be uni-axially pressed in a steel die.

**[00140]** The doped nanoparticles may be cold (i.e., at ambient temperature) iso-statically pressed at a pressure greater than or equal to 170 MPa and less than or equal to 240 MPa, greater than or equal to 170 MPa and less than or equal to 220 MPa, greater than or equal to 170 MPa and less than or equal to 200 MPa, greater than or equal to 190 MPa and less than or equal to 240 MPa, greater than or equal to 190 MPa and less than or equal to 220 MPa, or even greater than or equal to 190 MPa and less than or equal to 200 MPa, or any and all sub-ranges formed from any of these endpoints. The doped nanoparticles may be cold iso-statically pressed in an iso-pressing sheath.

[00141] The resulting preform may be any shape and have any dimension to ensure that the resulting transparent ceramic substrate is suitable for its intended purpose, such as a doped ceramic optical device as described herein.

[00142] Referring back to FIG. 1, the method 100 continues at block 104 with pre-sintering the preform to form a pre-sintered preform. In embodiments, the pre-sintering of block 104 may be conducted in ambient air, such as in a box furnace, or in a vacuum.

[00143] Referring back to FIG. 1 and now to FIG. 7A and 7B, the pre-sintering of block 104 includes two steps, a first pre-sintering step 104a and a second pre-sintering step 104b. The two-step pre-sintering described herein achieves reduced porosity by increasing density via reduced grain growth while maintaining grain boundary diffusion.

[00144] In embodiments, the first pre-sintering step 104a may comprise heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature to initiate grain boundary diffusion of the crystalline structure of the preform, which initiates densification and eventual sintering. In embodiments, the first furnace temperature may be greater than or equal to 1450 °C and less than or equal to 1600 °C. In embodiments, the first furnace temperature may be greater than or equal to 1450 °C, greater than or equal to 1475 °C, or even greater than or equal to 1500 °C. In embodiments, the first furnace temperature may be less than or equal to 1600 °C, less than or equal to 1575 °C, or even less than or equal to 1550 °C. In embodiments, the first furnace temperature may be greater than or equal to 1450 °C and less than or equal to 1600 °C, greater than or equal to 1450 °C and less than or equal to 1575 °C, greater than or equal to 1450 °C and less than or equal to 1550 °C, greater than or equal to 1475 °C and less than or equal to 1600 °C, greater than or equal to 1475 °C and less than or equal to 1575 °C, greater than or equal to 1475 °C and less than or equal to 1550 °C, greater than or equal to 1500 °C and less than or equal to 1600 °C, greater than or equal to 1500 °C and less than or equal to 1575 °C, or even greater than or equal to 1500 °C and less than or equal to 1550 °C, or any and all sub-ranges formed from any of these endpoints.

[00145] A ramp rate to the first furnace temperature may be limited (e.g., less than or equal to 10 °C/min) to prevent trapped gas pores inside the grains. Accordingly, in embodiments, the ramping to the first furnace temperature may be at a ramp rate greater than or equal to 2 °C/min and less than or equal to 10 °C/min. In embodiments, the ramp rate may be greater than or equal to 2 °C/min. In embodiments, the ramp rate may be less than or equal to 10 °C/min, less than or equal

to 8 °C/min, less than or equal to 6 °C/min, or even less than or equal to 4 °C/min. In embodiments, the ramp rate may be greater than or equal to 2 °C/min and less than or equal to 10 °C/min, greater than or equal to 2 °C/min and less than or equal to 8 °C/min, greater than or equal to 2 °C/min and less than or equal to 6 °C/min, or even greater than or equal to 2 °C/min and less than or equal to 4 °C/min, or any and all sub-ranges formed from any of these endpoints.

**[00146]** In embodiments, the second pre-sintering step 104b may comprise heating the preform at a second furnace temperature to form a pre-sintered preform. During the first pre-sintering step 104a, in addition to grain boundary diffusion, the grains of the crystalline structure of the preform are growing. However, too large of an average grain size (e.g., greater than 50  $\mu\text{m}$ ) may reduce density, thereby increasing scattering and interfering with optical transparency. As such, the furnace temperature at which the preform is heated may be lowered from a first furnace temperature to a second furnace temperature to maintain grain boundary diffusion while suppressing grain growth. In embodiments, the method may comprise reducing the furnace temperature from the first furnace temperature to the second furnace temperature after the first furnace temperature is reached such that the preform is not held for a time period greater than 10 seconds at the first furnace temperature. It may be desirable to not hold the preform at the first temperature to prevent further grain growth.

**[00147]** In embodiments, the second furnace temperature may be greater than or equal to 1350 °C and less than or equal to 1500 °C. In embodiments, the second furnace temperature may be greater than or equal to 1350 °C, greater than or equal to 1375 °C, greater than or equal to 1400 °C, or even greater than or equal to 1425 °C. In embodiments, the second furnace temperature may be less than or equal to 1500 °C, less than or equal to 1475 °C, or even less than or equal to 1450 °C. In embodiments, the second furnace temperature may be greater than or equal to 1350 °C and less than or equal to 1500 °C, greater than or equal to 1350 °C and less than or equal to 1475 °C, greater than or equal to 1350 °C and less than or equal to 1450 °C, greater than or equal to 1375 °C and less than or equal to 1500 °C, greater than or equal to 1375 °C and less than or equal to 1475 °C, greater than or equal to 1375 °C and less than or equal to 1450 °C, greater than or equal to 1400 °C and less than or equal to 1500 °C, greater than or equal to 1400 °C and less than or equal to 1475 °C, greater than or equal to 1400 °C and less than or equal to 1450 °C, greater than or equal to 1425 °C and less than or equal to 1500 °C, greater than or equal to 1425 °C and

less than or equal to 1475 °C, or even greater than or equal to 1425 °C and less than or equal to 1450 °C, or any and all sub-ranges formed from any of these endpoints.

**[00148]** In embodiments, the preform may held at the furnace second temperature for a time period greater than or equal to 10 hours and less than or equal to 120 hours to ensure sufficient grain bound diffusion to minimize the residue porosity and maximize the density. In embodiments, the preform may held at the second furnace temperature for a time period greater than or equal to 10 hours, greater than or equal to 15 hours, or even greater than or equal to 20 hours. In embodiments, the preform may held at the second furnace temperature for a time period less than or equal to 120 hours, less than or equal to 100 hours, less than or equal to 80 hours, less than or equal to 60 hours, or even less than or equal to 40 hours. In embodiments, the preform may held at the second furnace temperature for a time period greater than or equal to 10 hours and less than or equal to 120 hours, greater than or equal to 10 hours and less than or equal to 100 hours, greater than or equal to 10 hours and less than or equal to 80 hours, greater than or equal to 10 hours and less than or equal to 60 hours, greater than or equal to 10 hours and less than or equal to 40 hours, greater than or equal to 15 hours and less than or equal to 120 hours, greater than or equal to 15 hours and less than or equal to 100 hours, greater than or equal to 15 hours and less than or equal to 80 hours, greater than or equal to 15 hours and less than or equal to 60 hours, greater than or equal to 15 hours and less than or equal to 40 hours, greater than or equal to 20 hours and less than or equal to 120 hours, greater than or equal to 20 hours and less than or equal to 100 hours, greater than or equal to 20 hours and less than or equal to 80 hours, greater than or equal to 20 hours and less than or equal to 60 hours, or even greater than or equal to 20 hours and less than or equal to 40 hours, or any and all sub-ranges formed from any of these endpoints.

**[00149]** In embodiments, the furnace temperature may be reduced from the first furnace temperature to a second furnace temperature at a temperature reduction rate greater than or equal to 8 °C/min and less than or equal to 50 °C/min. In embodiments, the temperature reduction rate may be greater than or equal to 8 °C/min, greater than or equal to 12 °C/min, greater than or equal to 16 °C/min, or even greater than or equal to 20 °C/min. In embodiments, the temperature reduction rate may be less than or equal to 50 °C/min, less than or equal to 40 °C/min, or even less than or equal to 30 °C/min. In embodiments, the temperature reduction rate may be greater than or equal to 8 °C/min and less than or equal to 50 °C/min, greater than or equal to 8 °C/min and less than or equal to 40 °C/min, greater than or equal to 8 °C/min and less than or equal to 30

°C/min, greater than or equal to 12 °C/min and less than or equal to 50 °C/min, greater than or equal to 12 °C/min and less than or equal to 40 °C/min, greater than or equal to 12 °C/min and less than or equal to 30 °C/min, greater than or equal to 16 °C/min and less than or equal to 50 °C/min, greater than or equal to 16 °C/min and less than or equal to 40 °C/min, greater than or equal to 16 °C/min and less than or equal to 30 °C/min, greater than or equal to 20 °C/min and less than or equal to 50 °C/min, greater than or equal to 20 °C/min and less than or equal to 40 °C/min, or even greater than or equal to 20 °C/min and less than or equal to 30 °C/min, or any and all sub-ranges formed from any of these endpoints.

**[00150]** As discussed herein, the two-step pre-sintering described herein reduces grain growth while maintaining grain boundary diffusion. As such, the reduction rate from the first furnace temperature to the second furnace temperature may depend on the first furnace temperature and/or the second furnace temperature. For example, if the first furnace temperature is relatively high, it may be desirable to reduce from the first furnace temperature to the second furnace temperature relatively quickly.

**[00151]** In embodiments, as depicted in FIG. 7A, the furnace and the pre-sintered preform therein may be allowed to naturally cool, which may be dictated by the functions of the furnace within which the pre-sintering has occurred.

**[00152]** The pre-sintered preform may have a minimum relative density (e.g., greater than or equal to 92%) to ensure that the pre-sintered preform may be properly subjected to pressing and sintering to form a transparent ceramic substrate having desirable properties. Accordingly, in embodiments, the pre-sintered preform may have a relative density greater than or equal to 92%, greater than or equal to 94%, or even greater than or equal to 96%.

**[00153]** Referring back to FIG. 1, the method continues at block 106 with pressing and sintering the pre-sintered preform to form the transparent ceramic substrate. In embodiments, the pressing and sintering the pre-sintered preform may comprise hot iso-statically pressing the pre-sintered preform. In embodiments, the pre-sintered preform may be hot iso-statically pressed at a pressure greater than or equal to 170 MPa and less than or equal to 240 MPa, greater than or equal to 170 MPa and less than or equal to 220 MPa, greater than or equal to 170 MPa and less than or equal to 200 MPa, greater than or equal to 190 MPa and less than or equal to 240 MPa, greater than or equal to 190 MPa and less than or equal to 220 MPa, or even greater than or equal to 190 MPa and less than or equal to 200 MPa, or any and all sub-ranges formed from any of these endpoints. In

embodiments, the pre-sintered preform may be hot iso-statically pressed at one or more furnace temperatures greater than or equal to 1350 °C to and less than or equal to 1650 °C, greater than or equal to 1350 °C to and less than or equal to 1625 °C, greater than or equal to 1350 °C to and less than or equal to 1600 °C, greater than or equal to 1350 °C to and less than or equal to 1575 °C, greater than or equal to 1350 °C to and less than or equal to 1560 °C, greater than or equal to 1375 °C to and less than or equal to 1650 °C, greater than or equal to 1375 °C to and less than or equal to 1625 °C, greater than or equal to 1375 °C to and less than or equal to 1600 °C, greater than or equal to 1375 °C to and less than or equal to 1575 °C, greater than or equal to 1375 °C to and less than or equal to 1560 °C, greater than or equal to 1400 °C to and less than or equal to 1650 °C, greater than or equal to 1400 °C to and less than or equal to 1625 °C, greater than or equal to 1400 °C to and less than or equal to 1600 °C, greater than or equal to 1400 °C to and less than or equal to 1575 °C, greater than or equal to 1400 °C to and less than or equal to 1560 °C, greater than or equal to 1430 °C to and less than or equal to 1650 °C, greater than or equal to 1430 °C to and less than or equal to 1625 °C, greater than or equal to 1430 °C to and less than or equal to 1600 °C, greater than or equal to 1430 °C to and less than or equal to 1575 °C, or even greater than or equal to 1430 °C to and less than or equal to 1560 °C, or any and all sub-ranges formed from any of these endpoints.

**[00154]** Referring back to FIG. 1, the method 100 may optionally include, prior to block 102 of pressing the doped nanoparticles to form a preform, block 108 with sieving the doped nanoparticles through a sieve. Sieving the nanoparticles increases density by reducing the size of agglomerates of nanoparticles, which improves packing of the nanoparticles. Additionally, sieving may change the particle size distribution of the particles from bi-modal to tri-modal. While not wishing to be bound by theory, tri-modal particles have a higher theoretical packing density of 95.7% compared to 84% in the case of bi-modal configuration. Thus, subjecting the nanoparticles to sieving as described herein may improve the packing density of the nanoparticles during pressing.

**[00155]** In embodiments, the sieve may comprise a mesh size greater than or equal to 10 µm and less than or equal to 500 µm to ensure reduced size of the agglomerates of the nanoparticles. In embodiments, the mesh size may be greater than or equal to 10 µm, greater than or equal to 25 µm, or even greater than or equal to 50 µm. In embodiments, the mesh size may be less than or equal to 500 µm, less than or equal to 400 µm, less than or equal to 300 µm, less than or equal to 200 µm, or even less than or equal to 100 µm. In embodiments, the sieve may comprise a mesh

size greater than or equal to 10  $\mu\text{m}$  and less than or equal to 500  $\mu\text{m}$ , greater than or equal to 10  $\mu\text{m}$  and less than or equal to 400  $\mu\text{m}$ , greater than or equal to 10  $\mu\text{m}$  and less than or equal to 300  $\mu\text{m}$ , greater than or equal to 10  $\mu\text{m}$  and less than or equal to 200  $\mu\text{m}$ , greater than or equal to 10  $\mu\text{m}$  and less than or equal to 100  $\mu\text{m}$ , greater than or equal to 25  $\mu\text{m}$  and less than or equal to 500  $\mu\text{m}$ , greater than or equal to 25  $\mu\text{m}$  and less than or equal to 400  $\mu\text{m}$ , greater than or equal to 25  $\mu\text{m}$  and less than or equal to 300  $\mu\text{m}$ , greater than or equal to 25  $\mu\text{m}$  and less than or equal to 200  $\mu\text{m}$ , greater than or equal to 25  $\mu\text{m}$  and less than or equal to 100  $\mu\text{m}$ , greater than or equal to 50  $\mu\text{m}$  and less than or equal to 500  $\mu\text{m}$ , greater than or equal to 50  $\mu\text{m}$  and less than or equal to 400  $\mu\text{m}$ , greater than or equal to 50  $\mu\text{m}$  and less than or equal to 300  $\mu\text{m}$ , greater than or equal to 50  $\mu\text{m}$  and less than or equal to 200  $\mu\text{m}$ , or even greater than or equal to 50  $\mu\text{m}$  and less than or equal to 100  $\mu\text{m}$ , or any and all sub-ranges formed from any of these endpoints.

**[00156]** Generally, a hard grinding tool, such as an agate pestle and mortar, may be used to break agglomeration of nanoparticles. However, using a hard grinding tool to break apart as-synthesized nanoparticles may also initiate irregular packing of the doped nanoparticles. Accordingly, in embodiments, the sieving comprises passing the doped nanoparticles through a mesh. The mesh may be made of a relatively soft material, as compared to a hard grinding tool. For example, in embodiments, the sieve may comprise a mesh comprising nylon, acrylic, polyester, polyvinyl chloride, or combinations thereof.

**[00157]** In embodiments, a yield of the doped nanoparticles after sieving may be greater than or equal to 80% and less than or equal to 90%. The yield of doped nanoparticles after sieving may depend on the mesh size.

**[00158]** The doped nanoparticles may be sieved using a solvent, such as ethanol and/or deionized water.

**[00159]** Referring back to FIG. 1, as an alternative to block 108 with sieving the doped nanoparticles through a sieve, the method 100 may optionally include, prior to block 102 of pressing the doped nanoparticles to form a preform, block 110 with milling the doped nanoparticles. Milling the nanoparticles increases density by reducing the size of agglomerates of nanoparticles, which improves packing of the nanoparticles. Although shown as alternative steps, in embodiments, milling may be conducted in addition to sieving.

**[00160]** In embodiments, the milling the doped nanoparticles may comprise vibrational milling using milling media. In embodiments, the milling media may comprise yttria stabilized milling

media (e.g., YTZ<sup>®</sup> grinding media manufactured by Tosoh Corporation, Tokyo, Japan), aluminum oxide milling media, or combinations thereof. In embodiments, the milling media may comprise a diameter greater than or equal to 1 mm and less than or equal to 3 mm, greater than or equal to 1 mm and less than or equal to 2.5 mm, greater than or equal to 1 mm and less than or equal to 2 mm, greater than or equal to 1.5 mm and less than or equal to 3 mm, greater than or equal to 1.5 mm and less than or equal to 2.5 mm, or even greater than or equal to 1.5 mm and less than or equal to 2 mm, or any and all sub-ranges formed from any of these endpoints.

**[00161]** In embodiments, additional materials may be added before or during milling, for example, ethanol solvents, 1-butanol, propylene glycol, organophosphate, deionized water, or combinations thereof. The doped nanoparticles may be milled for a time period greater than or equal to 12 hours and less than or equal to 48 hours, greater than or equal to 12 hours and less than or equal to 32 hours, greater than or equal to 12 hours and less than or equal to 36 hours, greater than or equal to 12 hours and less than or equal to 30 hours, greater than or equal to 18 hours and less than or equal to 48 hours, greater than or equal to 18 hours and less than or equal to 32 hours, greater than or equal to 18 hours and less than or equal to 36 hours, greater than or equal to 18 hours and less than or equal to 30 hours, greater than or equal to 24 hours and less than or equal to 48 hours, greater than or equal to 24 hours and less than or equal to 32 hours, greater than or equal to 24 hours and less than or equal to 36 hours, or even greater than or equal to 24 hours and less than or equal to 30 hours, or any and all sub-ranges formed from any of these endpoints.

**[00162]** The milling disperses doped nanoparticles into a slurry. In embodiments, the slurry may be allowed to evaporate, such as in a fume hood, for a period of time sufficient to form a ceramic cake. In embodiments, the ceramic cake may be broken apart, such as with an agate pestle and mortar, to form the milled nanoparticles.

**[00163]** Referring now to FIG. 8, another method of forming a transparent ceramic substrate is shown at 150. The method 150 begins at block 152 or block 154 with subjecting doped nanoparticles to sieving through a sieve or milling. Although shown as alternative steps, in embodiments, milling may be conducted in addition to sieving.

**[00164]** The doped nanoparticles with respect to method 150 may be the same as or similar to the doped nanoparticles described herein with respect to method 100 shown in FIG. 1.

**[00165]** The sieving the doped nanoparticles through a sieve with respect to method 150 may be the same as or similar to the sieving the doped nanoparticles described herein as block 108 of method 100 shown in FIG. 1.

**[00166]** The milling the doped nanoparticles with respect to method 150 may be the same as or similar to the milling the doped nanoparticles described herein as block 110 of method 100 shown in FIG. 1.

**[00167]** Referring back to FIG. 8, the method 150 continues at block 156 with pressing the doped nanoparticles to form a preform. The pressing the doped nanoparticles with respect to method 150 may be the same as or similar to the pressing the doped nanoparticles described herein as block 102 of method 100 shown in FIG. 1.

**[00168]** Referring again to FIG. 8, the method 150 continues at block 158 with pre-sintering the preform to form a pre-sintered preform. In some embodiments, the pre-sintering the preform with respect to method 150 may be the same as or similar to the pre-sintering the preform described herein as block 104 of method 100 shown in FIG. 1. That is, the pre-sintering block 158 may comprise the two-step pre-sintering described herein. In other embodiments, the pre-sintering block 158 may comprise a single pre-sintering step. The single pre-sintering step may comprise heating the preform in a furnace by ramping a furnace temperature to a pre-sintering furnace temperature and holding the preform at the pre-sintering furnace temperature for a time period.

**[00169]** In embodiments, the pre-sintering furnace temperature may be greater than or equal to 1450 °C and less than or equal to 1650 °C. In embodiments, the pre-sintering furnace temperature may be greater than or equal to 1450 °C, greater than or equal to 1500 °C, or even greater than or equal to 1550 °C. In embodiments, the pre-sintering furnace temperature may be less than or equal to 1650 °C or even less than or equal to 1600 °C. In embodiments, the pre-sintering furnace temperature may be greater than or equal to 1450 °C and less than or equal to 1650 °C, greater than or equal to 1450 °C and less than or equal to 1600 °C, greater than or equal to 1500 °C and less than or equal to 1650 °C, greater than or equal to 1500 °C and less than or equal to 1600 °C, greater than or equal to 1550 °C and less than or equal to 1650 °C, or even greater than or equal to 1550 °C and less than or equal to 1600 °C, or any and all sub-ranges formed from any of these endpoints.

**[00170]** In embodiments, the time period at which the preform is held at the pre-sintering furnace temperature may be greater than or equal to 1 hour and less than or equal to 10 hours. In

embodiments, the time period at which the preform is held at the pre-sintering furnace temperature may be greater than or equal to 1 hour or even greater than or equal to 2 hours. In embodiments, the time period at which the preform is held at the pre-sintering furnace temperature may be less than or equal to 10 hours, less than or equal to 8 hours, less than or equal to 6 hours, or even less than or equal to 4 hours. In embodiments, the time period at which the preform is held at the pre-sintering furnace temperature may be greater than or equal to 1 hour and less than or equal to 10 hours, greater than or equal to 1 hour and less than or equal to 8 hours, greater than or equal to 1 hour and less than or equal to 6 hours, greater than or equal to 1 hour and less than or equal to 4 hours, greater than or equal to 2 hours and less than or equal to 10 hours, greater than or equal to 2 hours and less than or equal to 8 hours, greater than or equal to 2 hours and less than or equal to 6 hours, or even greater than or equal to 2 hours and less than or equal to 4 hours, or any and all sub-ranges formed from any of these endpoints.

[00171] Referring back to FIG. 8, the method 150 continues at block 160 with pressing and sintering the pre-sintered preform to form the transparent substrate. The pressing and sintering the pre-sintered preform with respect to method 150 may be the same as or similar to the pressing and sintering the pre-sintered preform as described herein as block 106 of method 100 shown in FIG. 1.

[00172] As described herein, the methods of forming transparent ceramic substrates disclosed herein reduce porosity by increasing density, which results in transparent ceramic substrates having reduced scattering and improved optical transparency.

[00173] In embodiments, a transparent ceramic substrate, formed according to the methods described herein, may have a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm. In embodiments, the transparent ceramic may have a transmitted scatter coefficient, as measured at 500 nm, less than or equal to 0.30 dB/mm, less than or equal to 0.25 dB/mm, less than or equal to 0.20 dB/mm, less than or equal to 0.15 dB/mm, or even less than or equal to 0.15 dB/mm.

[00174] In embodiments, a transparent ceramic substrate, formed according to the methods described herein, may have a total transmittance greater than or equal to 72%, as measured at 500 nm. In embodiments, the transparent ceramic substrate may have a total transmittance, as measured at 500 nm, greater than or equal to 72%, greater than or equal to 75%, greater than or equal to 78%, or even greater than or equal to 81%.

[00175] In embodiments, the transparent ceramic substrate, formed according to the methods described herein, may have a relative density greater than or equal to 99%. In embodiments, the transparent ceramic substrate may have a relative density greater than or equal to 99% or even greater than or equal to 99.5%.

[00176] As described herein, an average grain size greater than 50  $\mu\text{m}$  may reduce density, thereby increasing scattering and interfering with optical transparency. Accordingly, in embodiments, the transparent ceramic substrate may have an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ . In embodiments, the transparent ceramic substrate may have an average grain size greater than or equal to 0.5  $\mu\text{m}$ , greater than or equal to 0.7  $\mu\text{m}$ , or even greater than or equal to 1  $\mu\text{m}$ . In embodiments, the transparent ceramic substrate may have an average grain size less than or equal to 50  $\mu\text{m}$ , less than or equal to 25  $\mu\text{m}$ , less than or equal to 10  $\mu\text{m}$ , less than or equal to 5  $\mu\text{m}$ , or even less than or equal to 1  $\mu\text{m}$ . In embodiments, the transparent ceramic substrate may have an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ , greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 25  $\mu\text{m}$ , greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 10  $\mu\text{m}$ , greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 5  $\mu\text{m}$ , greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 1  $\mu\text{m}$ , greater than or equal to 0.7  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ , greater than or equal to 0.7  $\mu\text{m}$  and less than or equal to 25  $\mu\text{m}$ , greater than or equal to 0.7  $\mu\text{m}$  and less than or equal to 10  $\mu\text{m}$ , greater than or equal to 0.7  $\mu\text{m}$  and less than or equal to 5  $\mu\text{m}$ , greater than or equal to 0.7  $\mu\text{m}$  and less than or equal to 1  $\mu\text{m}$ , greater than or equal to 1  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ , greater than or equal to 1  $\mu\text{m}$  and less than or equal to 25  $\mu\text{m}$ , greater than or equal to 1  $\mu\text{m}$  and less than or equal to 10  $\mu\text{m}$ , or even greater than or equal to 1  $\mu\text{m}$  and less than or equal to 5  $\mu\text{m}$ , or any and all sub-ranges formed from any of these endpoints.

[00177] In embodiments, the transparent ceramic substrate, formed according to the methods described herein, may have a thickness greater than or equal to 1 mm and less than or equal to 20 mm. In embodiments, the transparent ceramic substrate may have a thickness greater than or equal to 1 mm. In embodiments, the transparent ceramic substrate may have a thickness less than or equal to 20 mm, less than or equal to 15 mm, less than or equal to 10 mm, less than or equal to 5 mm, or even less than or equal to 3 mm. In embodiments, the transparent ceramic substrate may have a thickness greater than or equal to 1 mm and less than or equal to 20 mm, greater than or equal to 1 mm and less than or equal to 15 mm, greater than or equal to 1 mm and less than or

equal to 10 mm, greater than or equal to 1 mm and less than or equal to 5 mm, or even greater than or equal to 1 mm and less than or equal to 3 mm, or any and all sub-ranges formed from any of these endpoints.

**[00178]** In embodiments, the transparent ceramic substrate, formed according to the methods described herein, may be a doped ceramic optical device. Referring now to FIG. 9, a quantum memory system is shown at 300. The quantum memory system 300 comprises a doped ceramic optical device 320, a magnetic field generation unit 340, a storage photon generator 370, and one or more pump lasers, such as a first pump laser 380a and a second pump laser 380b. The quantum memory system 300, the doped ceramic optical device 320, the magnetic field generation unit 340, the storage photon generator 370, the first pump laser 380a, and the second pump laser 380b may have the components, properties, and/or function as described in U.S. Patent No. 10,553,280, which is incorporated herein by reference in its entirety.

**[00179]** The doped ceramic optical device 320 may be formed from the doped nanoparticles described herein. Accordingly, the doped ceramic optical device 320 may comprise yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof.

**[00180]** The doped ceramic optical device 320 may comprise a variety of shapes and sizes to facilitate photon absorption and release. In embodiments, the doped ceramic optical device 320 may comprise a length extending between a first end 326 and a second end 328 greater than or equal to 1 cm and less than or equal to 50 cm, greater than or equal to 1 cm and less than or equal to 40 cm, greater than or equal to 1 cm and less than or equal to 30 cm, greater than or equal to 10 cm and less than or equal to 50 cm, greater than or equal to 10 cm and less than or equal to 40 cm, greater than or equal to 10 cm and less than or equal to 30 cm, greater than or equal to 20 cm and less than or equal to 50 cm, greater than or equal to 20 cm and less than or equal to 40 cm, or even greater than or equal to 20 cm and less than or equal to 30 cm, or any and all sub-ranges formed from any of these endpoints. In embodiments, the doped ceramic optical device 320 may have a cross sectional area greater than or equal to 0.01 mm<sup>2</sup> and less than or equal to 25 mm<sup>2</sup>, greater than or equal to 0.01 mm<sup>2</sup> and less than or equal to 20 mm<sup>2</sup>, greater than or equal to 0.01 mm<sup>2</sup> and less than or equal to 15 mm<sup>2</sup>, greater than or equal to 0.5 mm<sup>2</sup> and less than or equal to 25 mm<sup>2</sup>, greater than or equal to 0.5 mm<sup>2</sup> and less than or equal to 20 mm<sup>2</sup>, greater than or equal to 0.5 mm<sup>2</sup> and less than or equal to 15 mm<sup>2</sup>, greater than or equal 1 mm<sup>2</sup> and less than or equal to 25 mm<sup>2</sup>,

greater than or equal to 1 mm<sup>2</sup> and less than or equal to 20 mm<sup>2</sup>, greater than or equal to 1 mm<sup>2</sup> and less than or equal to 15 mm<sup>2</sup>, greater than or equal to 5 mm<sup>2</sup> and less than or equal to 25 mm<sup>2</sup>, greater than or equal to 5 mm<sup>2</sup> and less than or equal to 20 mm<sup>2</sup>, greater than or equal to 5 mm<sup>2</sup> and less than or equal to 15 mm<sup>2</sup>, greater than or equal to 10 mm<sup>2</sup> and less than or equal to 25 mm<sup>2</sup>, greater than or equal to 10 mm<sup>2</sup> and less than or equal to 20 mm<sup>2</sup>, or even greater than or equal to 10 mm<sup>2</sup> and less than or equal to 15 mm<sup>2</sup>, or any and all sub-ranges formed from any of these endpoints. In embodiments, the doped ceramic optical device 320 may have a width greater than or equal to 0.1 mm and less than or equal to 5 mm, greater than or equal to 0.1 mm and less than or equal to 4 mm, greater than or equal to 0.1 mm and less than or equal to 3 mm, greater than or equal to 0.5 mm and less than or equal to 5 mm, greater than or equal to 0.5 mm and less than or equal to 4 mm, greater than or equal to 0.5 mm and less than or equal to 3 mm, greater than or equal to 0.75 mm and less than or equal to 5 mm, greater than or equal to 0.75 mm and less than or equal to 4 mm, greater than or equal to 0.75 mm and less than or equal to 3 mm, greater than or equal to 1 mm and less than or equal to 5 mm, greater than or equal to 1 mm and less than or equal to 4 mm, greater than or equal to 1 mm and less than or equal to 3 mm, greater than or equal to 2 mm and less than or equal to 5 mm, greater than or equal to 2 mm and less than or equal to 4 mm, or even greater than or equal to 2 mm and less than or equal to 3 mm, or any and all sub-ranges formed from any of these endpoints.

**[00181]** The quantum memory system 300 is structurally configured to store and release one or more storage photons. Referring now to FIG. 10, when the doped ceramic optical device 320 is positioned within the magnetic field of the magnetic field generation unit 340 and the pump lasers 180a, 180b have irradiated the doped ceramic optical device 320 to generate the shaped spectral structure within a rare-earth element dopant 330, a ground state of the superposition of the shaped spectral structure of the rare-earth element dopant 330 is split such that each superposition of the shaped spectral structure of the rare-earth element dopant 330 comprises a first split ground state  $G_1$ , a second split ground state  $G_2$  and an excited energy state  $E_1$ . By splitting the ground state of the superposition of the shaped spectral structure of the rare-earth element dopant 330, the superposition of the shaped spectral structure may be transferred into the second ground state  $G_2$  to store the storage photon within the doped ceramic optical device 330.

**[00182]** The doped ceramic optical device 320 doped with the rare-earth element dopant 330 is structurally and compositionally configured to absorb and store a storage photon emitted by the

storage photon generator 370. For example, the shaped spectral structure may be generated in the doped ceramic optical device 320, for example, in the rare-earth element dopant 320, using one or more pump pulses output by the pump laser 380a, 380b.

**[00183]** Next, when the storage photon is traversing the doped ceramic optical device 320, the storage photon may transfer the superposition of the shaped spectral structure of the rare-earth element dopant 330 from the first split ground state  $G_1$  to the excited energy state  $E_1$ , as schematically shown in FIG. 10, to absorb the storage photon. Next, upon receipt of a first pump pulse output by the first pump laser 380 a, the first pump pulse may transfer the superposition of the shaped spectral structure of the rare-earth element dopant 330 from the excited energy state  $E_1$  into the second split ground state  $G_2$ , to store the storage photon.

**[00184]** Further, the doped ceramic optical device 320 doped with the rare-earth element dopant 130 is structurally and compositionally configured to release, on demand, the storage photon stored within the doped ceramic optical device 320. For example, upon receipt of a second pump pulse output by the second pump laser 380b, the superposition of the shaped spectral structure of the rare-earth element dopant 1330 is transferred from the second split ground state  $G_2$  back to the excited energy state  $E_1$ . Once in the excited energy state  $E_1$ , the superposition of the shaped spectral structure of the rare-earth element dopant 330 will automatically release the storage photon after a delay period, such that the storage photon exits the doped ceramic optical device 320, for example, the first end 326 of the doped ceramic optical device 320. For example, once in the excited energy state  $E_1$ , the shaped spectral structure of the rare-earth element dopant 330 will rephase, and after the delay period, the storage photon will exit the doped ceramic optical device 320. Moreover, the storage photon may exit the first end 326 of the doped ceramic optical device 320 when the second pump laser 380b emits the second pump pulse into to the second end 328 of the doped ceramic optical device 320 and the storage photon may exit the second end 328 of the doped ceramic optical device 320 when the second pump laser 380b emits the second pump pulse into the first end 326 of the doped ceramic optical device 320.

**[00185]** The delay period comprises a consistent, repeatable time period, thus, upon repeated operation, individual storage photons are released after the same delay period. Furthermore, different doped ceramic optical devices 320 may comprise the same or different delay periods. The quantum memory system 300 may be incorporated into one or more quantum communications

systems, such as quantum key generation systems, quantum telecommunications systems, or quantum internet systems.

[00186] Optical scattering due to porosity in the doped ceramic optical device 320 may cause scattering induced attenuation when photons traverse the doped ceramic optical device 320. Thus, reducing the porosity of the doped ceramic optical device 320, using the methods of forming a transparent ceramic substrate described herein, may reduce the attenuation rate of photons traversing the doped optical ceramic device 320, thereby improving the performance thereof.

### *Examples*

[00187] In order that various embodiments be more readily understood, reference is made to the following examples, which are intended to illustrate various embodiments of the transparent ceramic substrates described herein.

#### [00188] **Two-step Pre-Sintering**

[00189] Eight (8)  $\text{Y}_2\text{O}_3$  ceramic pellets were obtained via uniaxial pressing and cold iso-static pressing. The ceramic pellets were pre-sintered in air in a box furnace according to the pre-sintering cycles shown in Tables 1 and 2. The pre-sintered ceramic pellets were subjected to hot-isostatic pressing to form comparative ceramic pellets C1-C6 and example ceramic pellets E1 and E2.

[00190] Note that comparative ceramic pellets C1-C6 resulted from a single-step pre-sintering, whereas example ceramic pellets E1 and E3 results from a two-step pre-sintering.

[00191] Comparative ceramic pellets C1-C6 were formed by heating the pellets in the furnace by ramping to a furnace temperature at a ramp rate  $2.1\text{ }^\circ\text{C}/\text{min}$ . The pellets were not held at the furnace temperature. That is, immediately after reaching the furnace temperature, the furnace and the pellets were then allowed to naturally cool.

[00192] Example ceramic pellets E1 and E2 were formed by heating the pellets in the furnace by ramping the furnace temperature to a first furnace temperature at a ramp rate  $2.1\text{ }^\circ\text{C}/\text{min}$ . Immediately after reaching the first furnace temperature, the furnace temperature was reduced from the first furnace temperature to a second furnace temperature at a temperature reduction rate of  $8.3\text{ }^\circ\text{C}/\text{min}$ . The pellets were held at the second furnace temperature for 1,250 min. The furnace and the pellets were then allowed to naturally cool. FIGS. 11A and 11B show the pre-sintering cycle used to form example ceramic pellet E2.

[00193] Scanning electron microscope (SEM) images and grain size distribution of comparative ceramic pellets C1-C6 and example ceramic pellets E1 and E2 are shown in FIGS. 12-27. The corresponding average grain size and grain size distribution were collected from the SEM images.

[00194] **Table 1**

|                                 | <i>C1</i> | <i>C2</i> | <i>C4</i> | <i>C4</i> | <i>C5</i> | <i>C6</i> |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| <i>Furnace temperature (°C)</i> | 1650      | 1600      | 1550      | 1500      | 1450      | 1400      |

[00195] **Table 2**

|                                                | <i>E1</i> | <i>E2</i> |
|------------------------------------------------|-----------|-----------|
| <i>1<sup>st</sup> furnace temperature (°C)</i> | 1550      | 1500      |
| <i>2<sup>nd</sup> furnace temperature (°C)</i> | 1500      | 1450      |

[00196] A sintering trajectory of the ceramic pellets, prior to hot iso-static pressing, as average grain size, collected from the respective SEM images, as a function of relative density is shown in FIG. 28. A sintering trajectory of the ceramic pellets, prior to hot iso-static pressing, as average grain size as a function of  $\ln(1-D)$ , where D is the relative density, is shown in FIG. 29. Example ceramic pellets E1 and E2 had a higher relative density at lower average grain size as compared to comparative ceramic pellets C1-C6. As exemplified in FIGS. 28 and 29, a two-step pre-sintering results in higher density at a lower average grain size.

[00197] **Sieving**

[00198] Referring now to FIGS. 30-32, SEM images of  $Y_2O_3$  nanoparticles are shown. FIG. 30 shows as-synthesized  $Y_2O_3$  nanoparticles. FIG. 31 shows  $Y_2O_3$  nanoparticles after being subjected to sieving through a 105  $\mu m$  Nylon mesh cloth with ethanol and deionized water. FIG. 32 shows  $Y_2O_3$  nanoparticles after being subjected to sieving through a 52  $\mu m$  Nylon mesh cloth with ethanol and deionized water. As exemplified in FIGS. 30-32, the millimeter-scale agglomeration in as-synthesized nanoparticles may be broken into a micron-sized agglomeration using a sieving process as described herein.

[00199] Referring now to FIG. 33, the particle size distribution of the as-synthesized  $Y_2O_3$  nanoparticles and the sieved  $Y_2O_3$  nanoparticles is shown. As exemplified in FIG. 33, the particle size distribution mode was changed from bi-modal to tri-modal via sieving.

[00200] Example ceramic pellets E3-E6 were formed by subjecting the sieved nanoparticles to uniaxial pressing and cold iso-static pressing, pre-sintering at 1570 °C for 2 hours, and hot-isostatic pressing at 1510 °C at 207 MPa for 16 hours. Example ceramic pellets E3 and E4 were formed from the nanoparticles sieved through the 105 µm Nylon mesh cloth and example ceramic pellets E5 and E6 were formed from the nanoparticles sieved through the 52 µm Nylon mesh cloth. The scatter coefficient of examples ceramic pellets E3-E6 is discussed below.

[00201] **Milling**

[00202] 8 grams of Er doped Y<sub>2</sub>O<sub>3</sub> nanoparticles was mixed with 16 g ethanol in a Nalgene bottle. 50 grams of 2 mm yttria stabilized balls were added as milling media. The Nalgene bottle was sealed and loaded into a vibrational mill for a 24 hour milling treatment. The obtained ceramic slurry was then transferred to a glass beaker to evaporate the ethanol in a fume hood. The ceramic slurry on Day 0, 3, and 4 is shown in FIG. 34. As shown, on Day 4, the dry slurry formed a ceramic cake. On Day 5, as shown in FIG. 34, the ceramic cake was smashed with an agate pestle and mortar.

[00203] Example ceramic pellet E7 was formed by subjecting the milled nanoparticles to uniaxial pressing and cold iso-static pressing, pre-sintering at 1570 °C for 2 hours, and hot-isostatic pressing at 1510 °C at 207 MPa for 16 hours. The scatter coefficient of example ceramic pellet E7 is discussed below.

[00204] **Scatter Loss Comparison**

[00205] A comparative ceramic pellet C7 was formed by subjecting a Y<sub>2</sub>O<sub>3</sub> ceramic pellet, obtained via uniaxial pressing and cold iso-static pressing, to pre-sintering at 1520 °C for 2 hours followed by hot-isostatic pressing 1510 °C at 207 MPa for 16 hours.

[00206] Referring to FIG. 35, the transmitted scatter coefficients of comparative ceramic pellet C7 and example ceramic pellets E1 and E4-E7 as measured from 300 nm to 2400 nm are shown. Referring to FIG. 36, the transmitted scatter coefficients of comparative ceramic pellet C7 and example ceramic pellets E1 and E4-E7 as measured at 500 nm is shown. As exemplified in FIGS. 35 and 36, ceramic substrates formed according to the methods described herein exhibit reduced scattering as compared to ceramic substrates formed from conventional methods.

[00207] It will be apparent to those skilled in the art that various modifications and variations may be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus, it is intended that the specification cover the modifications and

variations of the various embodiments described herein provided such modification and variations come within the scope of the appended claims and their equivalents.

**CLAIMS**

1. A method of forming a transparent ceramic substrate, the method comprising:  
pressing doped nanoparticles to form a preform;  
pre-sintering the preform, wherein the pre-sintering comprises:  
a first pre-sintering step comprising heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature greater than or equal to 1450 °C and less than or equal to 1600 °C; and  
a second pre-sintering step comprising heating the preform at a second furnace temperature greater than or equal to 1350 °C and less than or equal to 1500 °C to form a pre-sintered preform; and  
pressing and sintering the pre-sintered preform to form the transparent ceramic substrate.
2. The method of claim 1, wherein the ramping to the first furnace temperature is at a ramp rate greater than or equal to 2 °C/min and less than or equal to 10 °C/min.
3. The method of claim 1 or claim 2, wherein the method further comprises reducing the furnace temperature from the first furnace temperature to the second furnace temperature after the first furnace temperature is reached such that the preform is not held for a time period at the first temperature greater than 10 seconds at the first furnace temperature.
4. The method of any one of claims 1-3, wherein the preform is held at the second furnace temperature for a time period greater than or equal to 10 hours and less than or equal to 120 hours.
5. The method of claim 3 or claim 4, wherein the furnace temperature is reduced from the first furnace temperature to the second furnace temperature at a temperature reduction rate greater than or equal to 8 °C/min and less than or equal to 50 °C/min.
6. The method of any one of claims 1-5, wherein the doped nanoparticles comprise rare-earth doped nanoparticles.

7. The method of claim 6, wherein the rare-earth doped nanoparticles comprise yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof.
8. The method of any one of claims 1-7, wherein the method further comprises, prior to the pressing the doped nanoparticles to form the preform, sieving the doped nanoparticles through a sieve.
9. The method of claim 8, wherein the sieve comprises a mesh size greater than or equal to 10  $\mu\text{m}$  and less than or equal to 500  $\mu\text{m}$ .
10. The method of claim 8 or claim 9, wherein the sieving comprises passing the doped nanoparticles through a mesh.
11. The method of claim 10, wherein the sieve comprises a mesh comprising nylon, acrylic, polyester, polyvinyl chloride, or combinations thereof.
12. The method of any one of claims 1-7, wherein the method further comprises, prior to the pressing the doped nanoparticles to form the preform, milling the doped nanoparticles.
13. The method of claim 12, wherein the milling the doped nanoparticles comprises vibrational milling using milling media.
14. The method of claim 13, wherein the milling media comprises yttria stabilized milling media, aluminum oxide milling media, or combinations thereof.
15. The method of any one of claims 1-14, wherein the pressing and sintering the pre-sintered preform comprises hot iso-statically pressing the pre-sintered preform.
16. The method of any one of claims 1-15, wherein the pressing the doped nanoparticles comprises uni-axially pressing the doped nanoparticles.

17. The method of any one of claims 1-16, wherein the pressing the doped nanoparticles comprises cold iso-statically pressing the doped nanoparticles.
18. The method of any one of claims 1-17, wherein the doped nanoparticles are formed by:  
mixing a matrix material, a plurality of rare-earth metal dopants, an organic precursor, and water to form a precursor mixture; and  
heating the precursor mixture to a heating temperature to induce thermal decomposition of the organic precursor and generate a chemical reaction between the matrix material and the plurality of rare-earth metal dopants to form the doped nanoparticles.
19. The method of any one of claims 1-17, wherein the doped nanoparticles are formed by:  
mixing a matrix material, a plurality of rare-earth metal dopants, and water to form a metal salt solution;  
heating the metal salt solution to form a heated metal salt solution; and  
mixing the heated metal salt solution with an organic precursor to form the doped nanoparticles.
20. A transparent ceramic substrate made by the method of any one of claims 1-19, wherein the transparent ceramic substrate has a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.
21. A transparent ceramic substrate of claim 20, wherein the transparent ceramic substrate has a total transmittance greater than or equal to 72%, as measured at 500 nm.
22. The transparent ceramic substrate of claim 20 of claim 21, wherein the transparent ceramic substrate has a relative density greater than or equal to 99%.
23. The transparent ceramic substrate any one of claims 20-22, wherein the transparent ceramic substrate has an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ .

24. The transparent ceramic substrate of any one of claims 20-23, wherein the transparent ceramic substrate has a thickness greater than or equal to 1 mm and less than or equal to 20 mm.
25. The transparent ceramic substrate of any one of claims 20-24, wherein the transparent ceramic substrate is a doped ceramic optical device.
26. A quantum memory system comprising the doped ceramic optical device of claim 25.
27. A method of forming a transparent ceramic substrate, the method comprising:  
subjecting doped nanoparticles to sieving through a sieve or milling;  
pressing the doped nanoparticles to form a preform;  
pre-sintering the preform to form a pre-sintered preform; and  
pressing and sintering the pre-sintered preform to form the transparent ceramic substrate.
28. The method of claim 27, wherein the sieve comprises a mesh size greater than or equal to 10  $\mu\text{m}$  and less than or equal to 500  $\mu\text{m}$ .
29. The method of claim 27 or claim 28, wherein the sieving comprises passing the doped nanoparticles through a mesh.
30. The method of claim 29, wherein the sieve comprises a mesh comprising nylon, acrylic, polyester, polyvinyl chloride, or combinations thereof.
31. The method of claim 27, wherein the milling the doped nanoparticles comprises vibrational milling using milling media.
32. The method of claim 31, wherein the milling media comprises yttria stabilized milling media, aluminum oxide milling media, or combinations thereof.
33. The method of any one of claims 27-32, wherein the doped nanoparticles comprise rare-earth doped nanoparticles.

34. The method of claim 33, wherein the rare-earth doped nanoparticles comprise yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof.
35. The method of any one of claims 27-34, wherein the pre-sintering comprises a single pre-sintering step, the single pre-sintering step comprising:
- heating the preform in a furnace by ramping a furnace temperature to a pre-sintering furnace temperature greater than or equal to 1450 °C and less than or equal to 1650 °C; and
  - holding the preform at the pre-sintering furnace temperature for a time period greater than or equal to 1 hour and less than or equal to 10 hours.
36. The method of any one of claims 27-34, wherein the pre-sintering comprises:
- a first pre-sintering step comprising heating the preform in a furnace by ramping a furnace temperature to a first furnace temperature greater than or equal to 1450 °C and less than or equal to 1600 °C; and
  - a second pre-sintering step comprising heating the preform at a second furnace temperature greater than or equal to 1350 °C and less than or equal to 1500 °C to form a pre-sintered preform.
37. The method of claim 36, wherein the ramping to the first furnace temperature is at a ramp rate greater than or equal to 2 °C/min and less than or equal to 10 °C/min.
38. The method of claim 36 or claim 37, wherein the method further comprises reducing the furnace temperature from the first furnace temperature to the second furnace temperature after the first furnace temperature is reached such that the preform is not held for a time period at the first temperature greater than 10 seconds at the first furnace temperature.
39. The method of any one of claims 36-38, wherein the preform is held at the second furnace temperature for a time period greater than or equal to 10 hours and less than or equal to 120 hours.
40. The method of claim 38 or claim 39, wherein the furnace temperature is reduced from the first furnace temperature to the second furnace temperature at a temperature reduction rate greater than or equal to 8 °C/min and less than or equal to 50 °C/min.

41. The method of any one of claims 27-40, wherein the pressing and sintering the pre-sintered preform comprises hot iso-statically pressing the pre-sintered preform.
42. The method of any one of claims 27-41, wherein the pressing the doped nanoparticles comprises uni-axially pressing the doped nanoparticles.
43. The method of any one of claims 27-42, wherein the pressing the doped nanoparticles comprises cold iso-statically pressing the doped nanoparticles.
44. The method of any one of claims 27-43, wherein the doped nanoparticles are formed by:  
mixing a matrix material, a plurality of rare-earth metal dopants, an organic precursor, and water to form a precursor mixture; and  
heating the precursor mixture to a heating temperature to induce thermal decomposition of the organic precursor and generate a chemical reaction between the matrix material and the plurality of rare-earth metal dopants to form the doped nanoparticles.
45. The method of any one of claims 27-43, wherein the doped nanoparticles are formed by:  
mixing a matrix material, a plurality of rare-earth metal dopants, and water to form a metal salt solution;  
heating the metal salt solution to form a heated metal salt solution; and  
mixing the heated metal salt solution with an organic precursor to form the doped nanoparticles.
46. A transparent ceramic substrate made by the method of any one of claims 27-45, wherein the transparent ceramic substrate has a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.
47. A transparent ceramic substrate of claim 46, wherein the transparent ceramic substrate has a total transmittance greater than or equal to 72%, as measured at 500 nm.

48. The transparent ceramic substrate of claim 46 of claim 47, wherein the transparent ceramic substrate has a relative density greater than or equal to 99%.
49. The transparent ceramic substrate any one of claims 46-48, wherein the transparent ceramic substrate has an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ .
50. The transparent ceramic substrate of any one of claims 46-49, wherein the transparent ceramic substrate has a thickness greater than or equal to 1 mm and less than or equal to 20 mm.
51. The transparent ceramic substrate of any one of claims 46-50, wherein the transparent ceramic substrate is a doped ceramic optical device.
52. A quantum memory system comprising the doped ceramic optical device of claim 51.
53. A quantum memory system comprising:  
a doped ceramic optical device, the doped ceramic optical device comprising:  
yttrium, zirconium, hafnium, erbium, scandium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, thulium, ytterbium, lutetium, or combinations thereof; and  
a transmitted scatter coefficient less than or equal to 0.30 dB/mm, as measured at 500 nm.
54. The quantum memory system of claim 53, wherein the doped ceramic optical device has a total transmittance greater than or equal to 72%, as measured at 500 nm.
55. The quantum memory system of claim 53 or claim 54, wherein the doped ceramic optical device has a relative density greater than or equal to 99%.
56. The quantum memory system of any one of claims 53-55, wherein the doped ceramic optical device has an average grain size greater than or equal to 0.5  $\mu\text{m}$  and less than or equal to 50  $\mu\text{m}$ .

57. The quantum memory system of any one of claims 53-56, wherein the doped ceramic optical device has a thickness greater than or equal to 1 mm and less than or equal to 20 mm.

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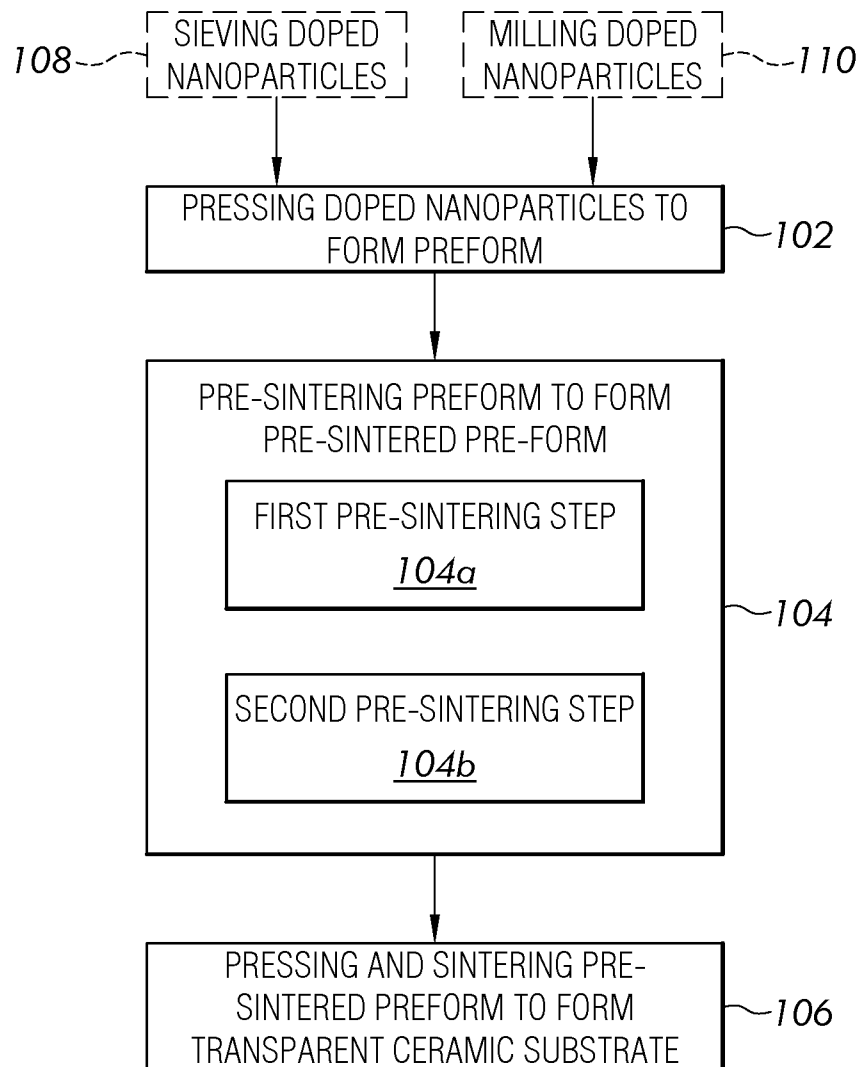
100  


FIG. 1

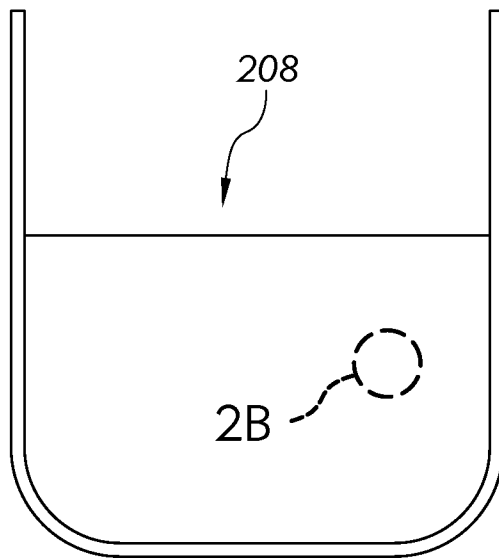


FIG. 2A

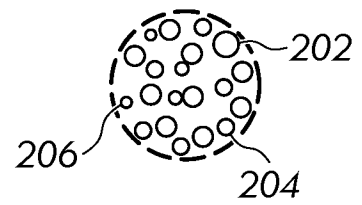


FIG. 2B

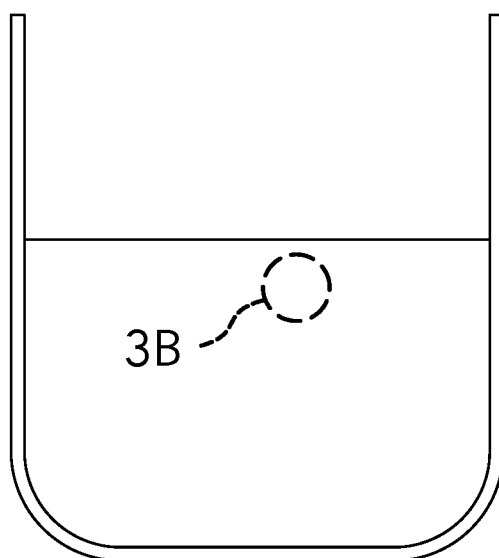


FIG. 3A

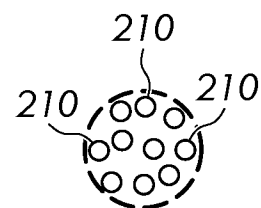


FIG. 3B

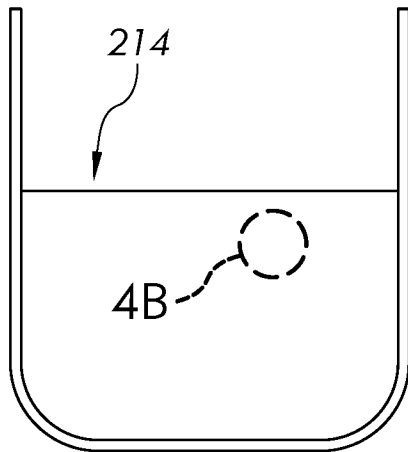


FIG. 4A

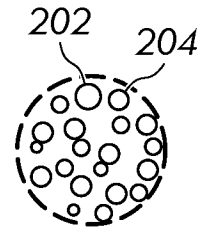


FIG. 4B

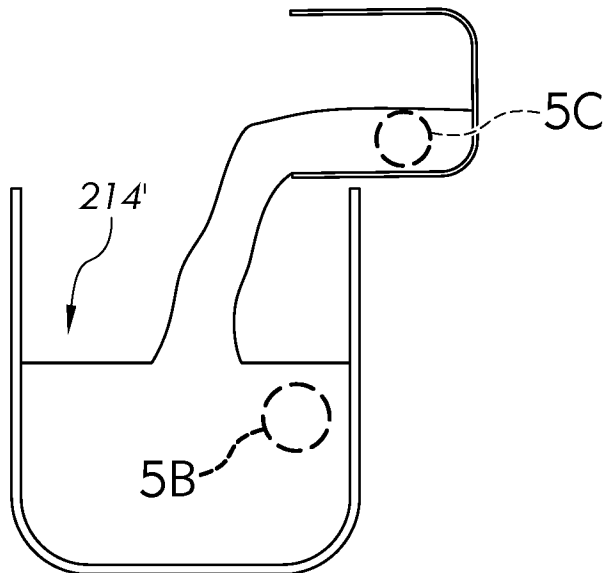


FIG. 5A

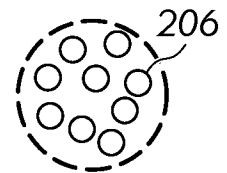


FIG. 5C

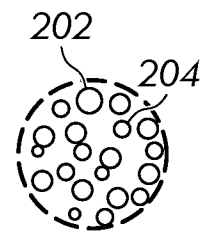


FIG. 5B

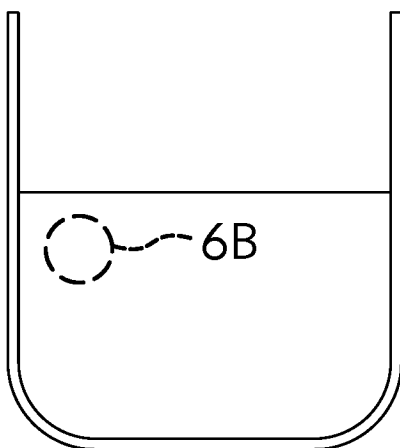


FIG. 6A

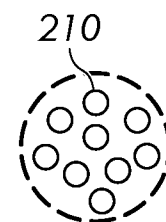


FIG. 6B

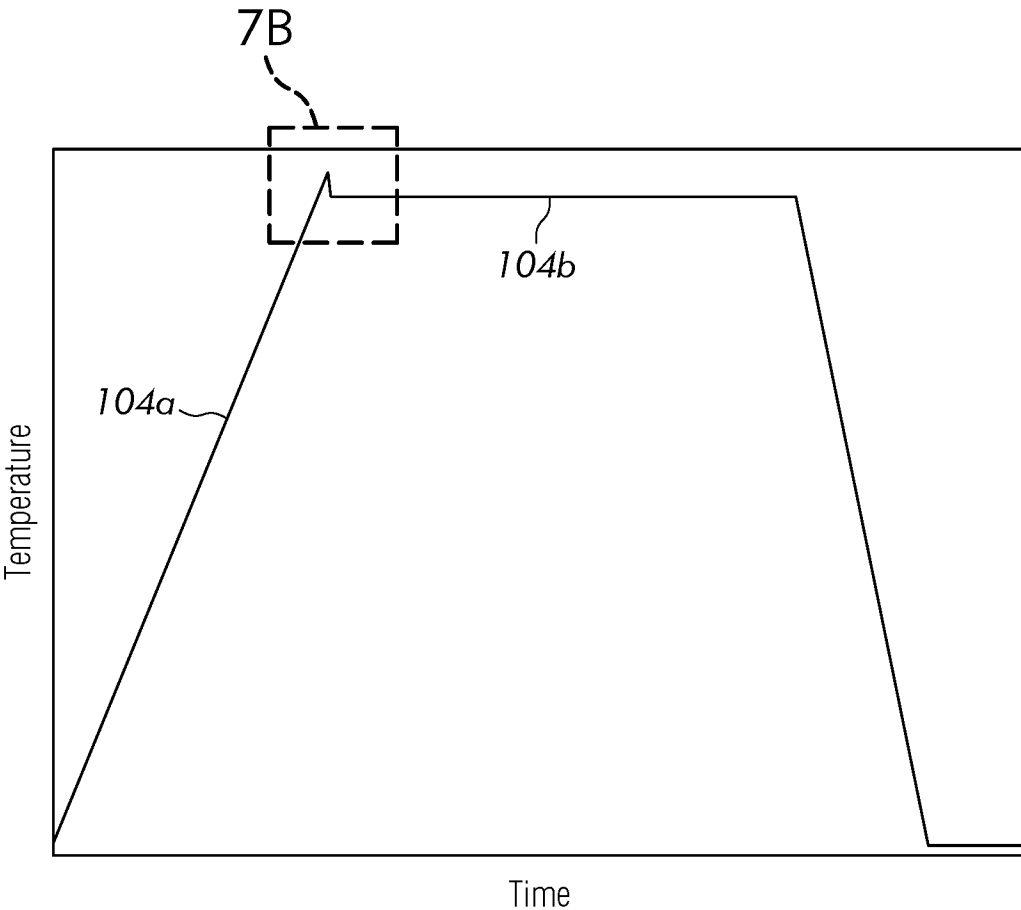


FIG. 7A

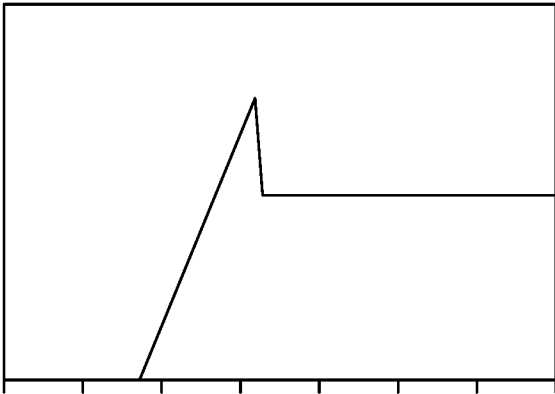


FIG. 7B

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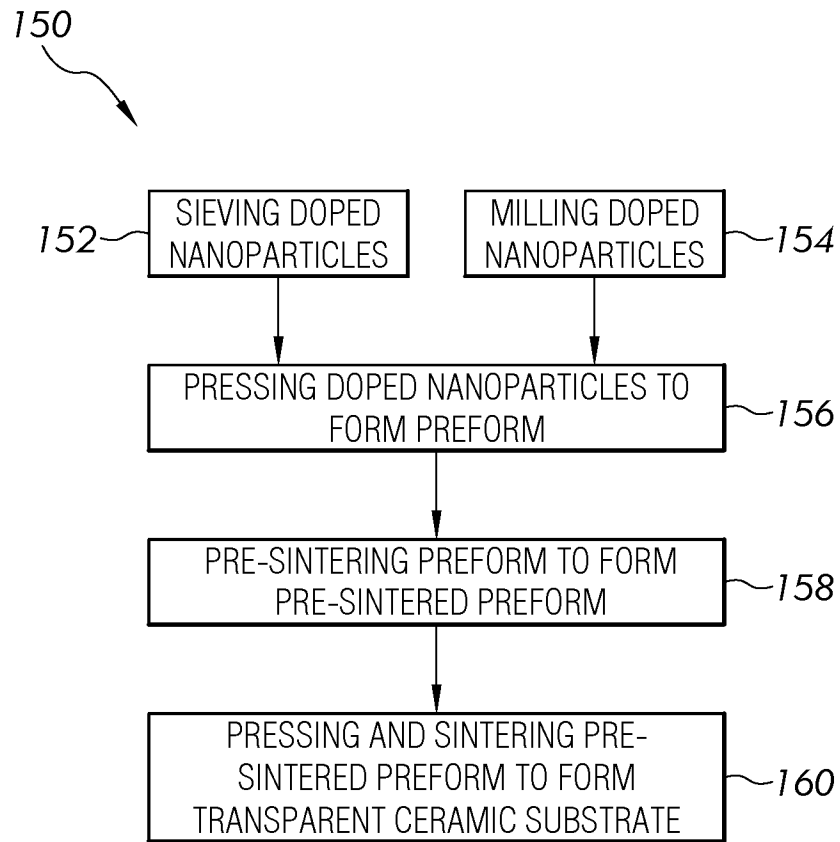


FIG. 8

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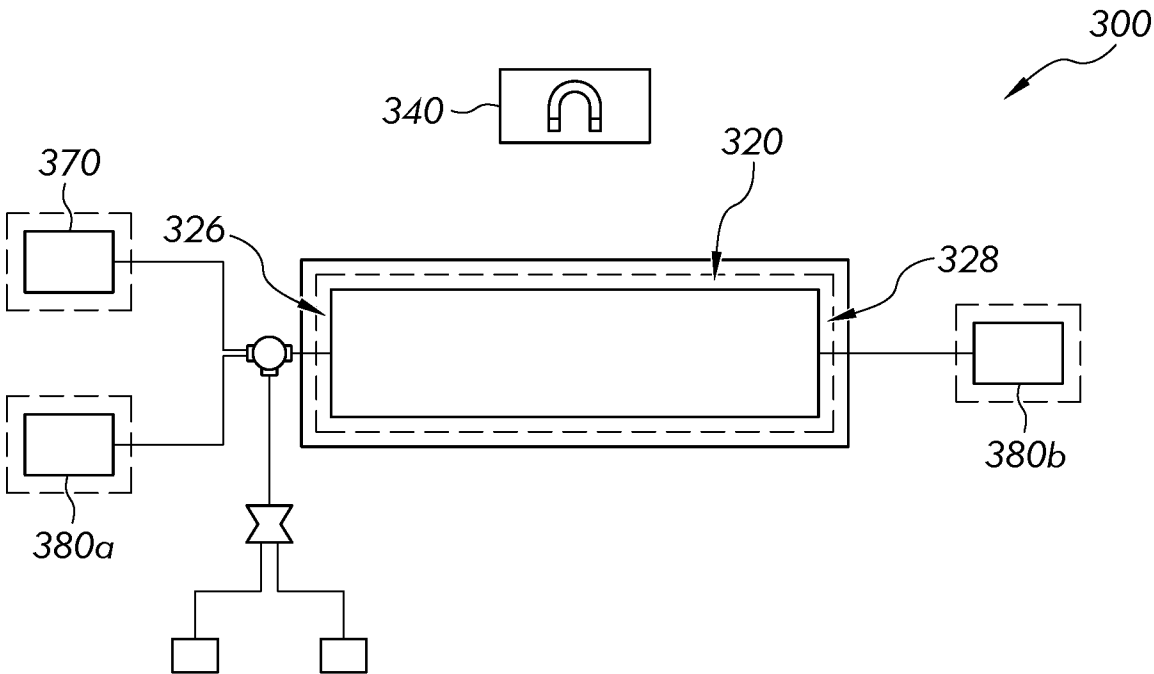


FIG. 9

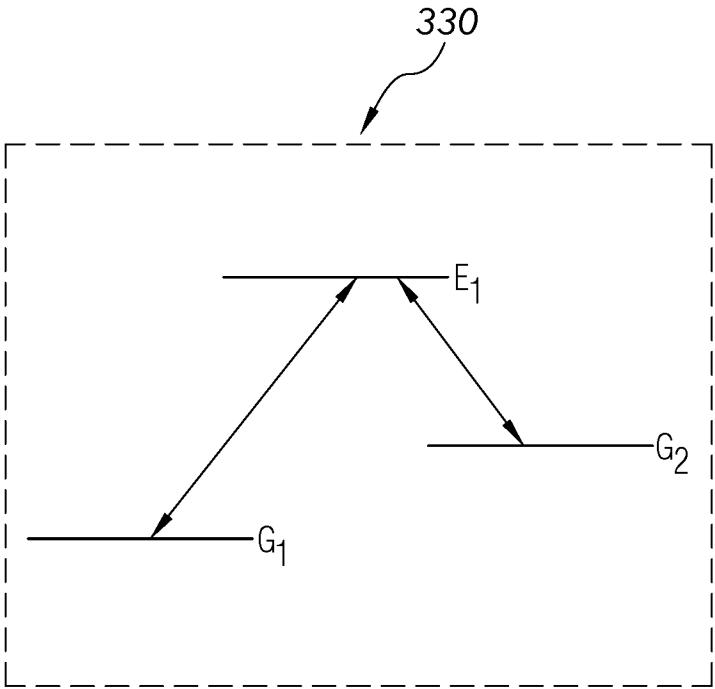


FIG. 10

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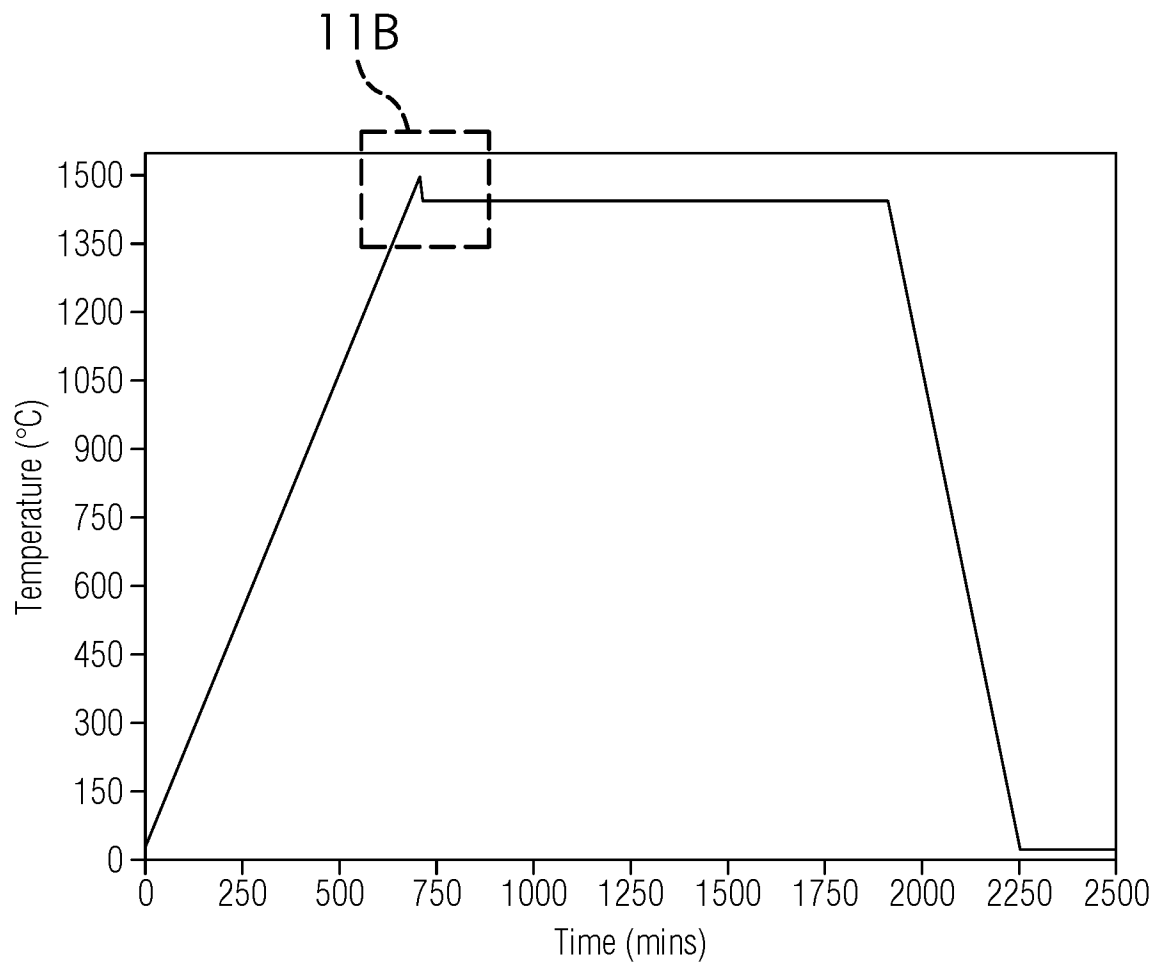


FIG. 11A

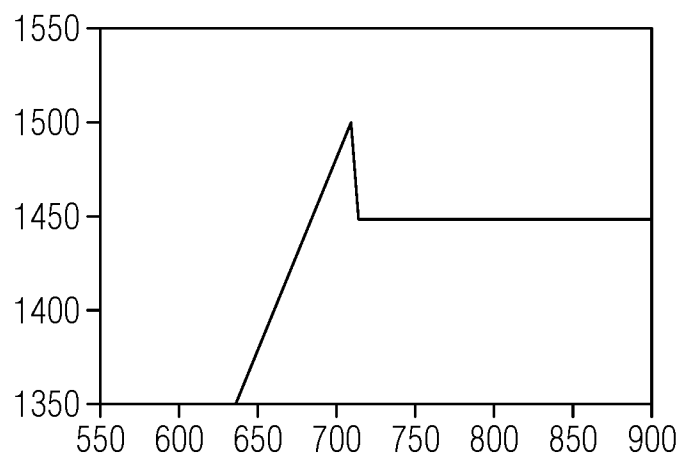


FIG. 11B

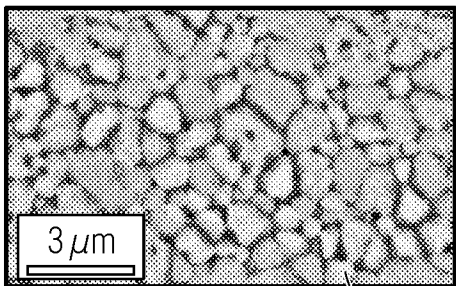


FIG. 12 C1

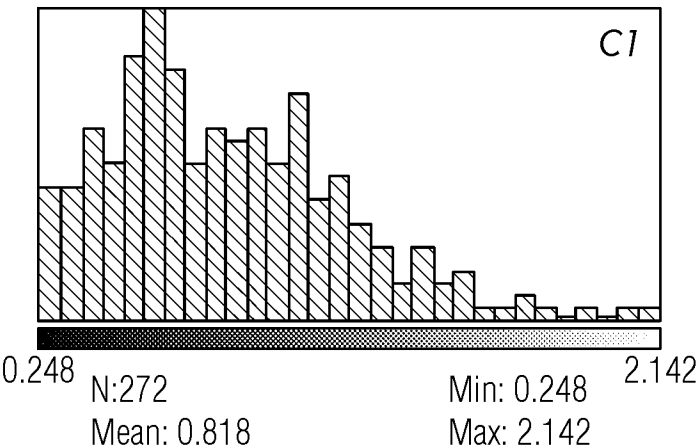


FIG. 13

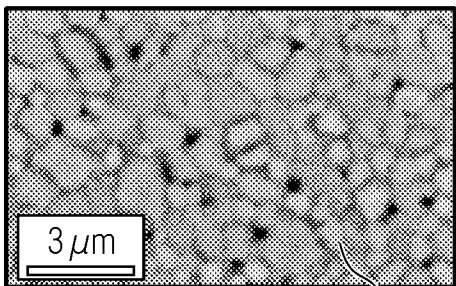


FIG. 14 C2

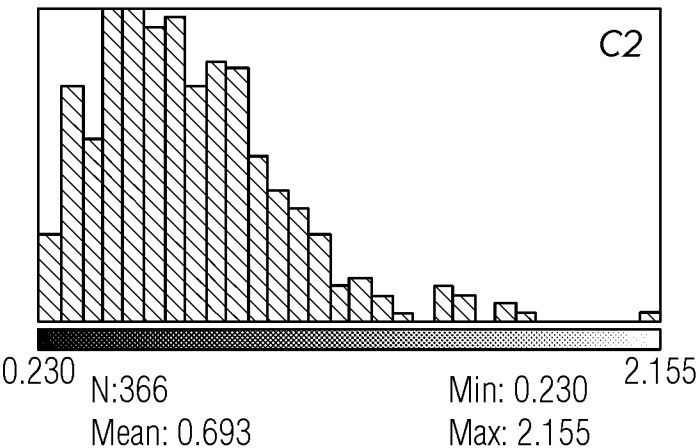


FIG. 15

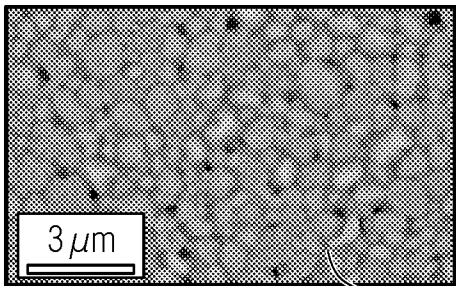


FIG. 16 C3

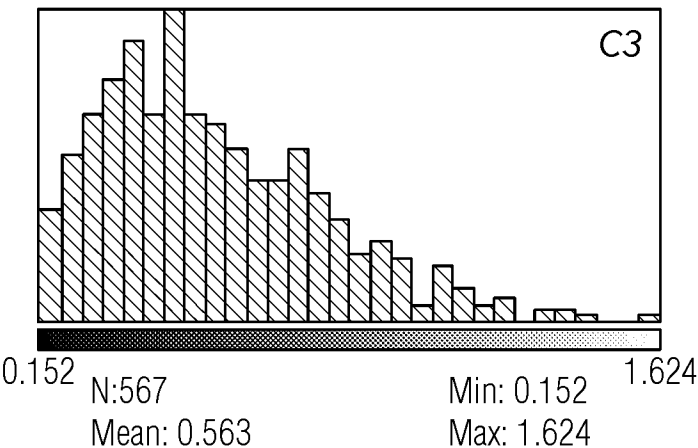


FIG. 17

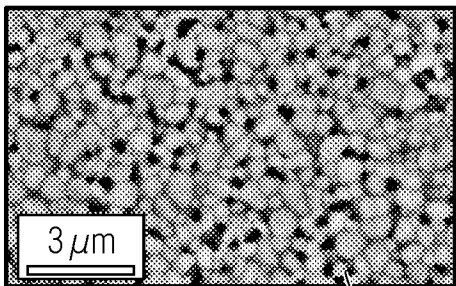


FIG. 18 C4

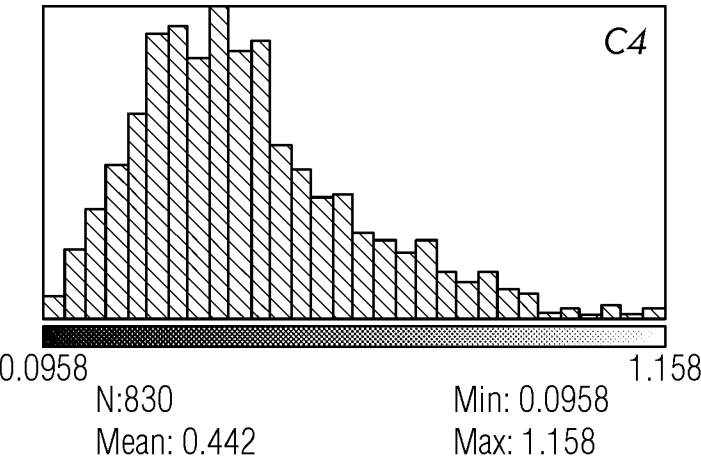


FIG. 19

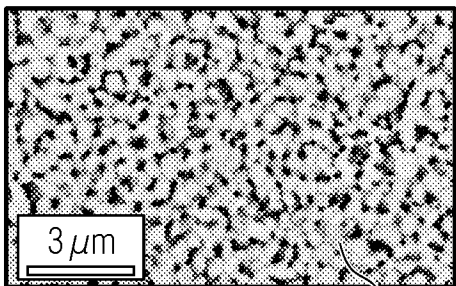


FIG. 20 C5

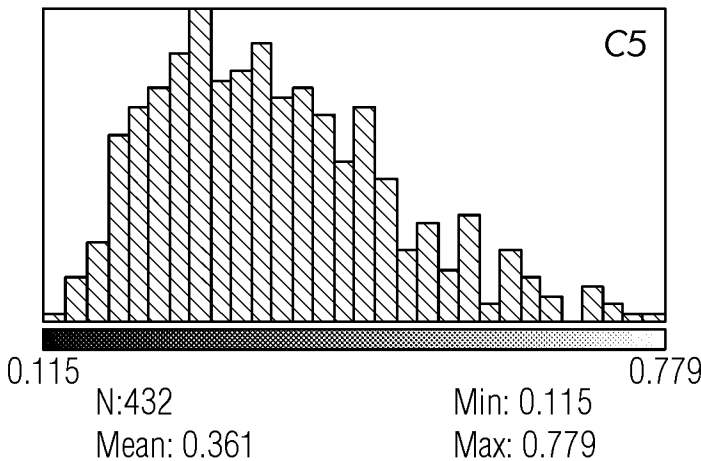


FIG. 21

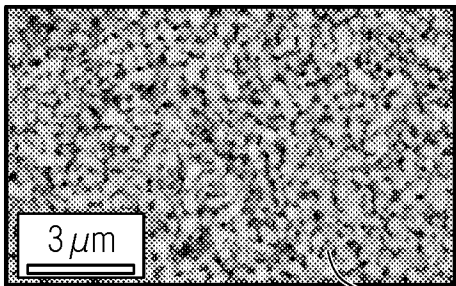


FIG. 22 C6

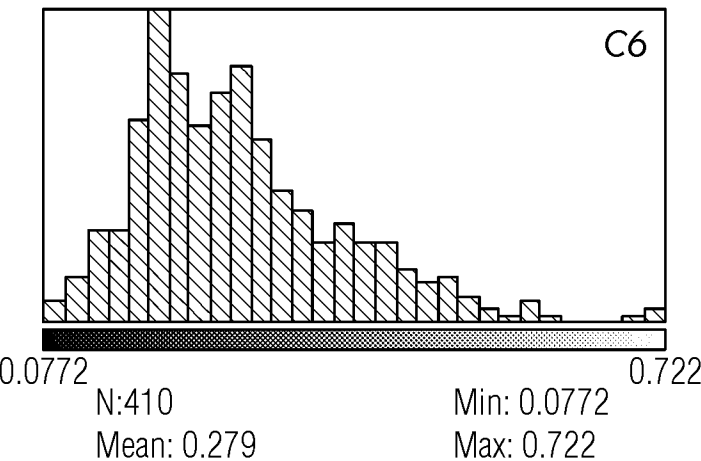


FIG. 23

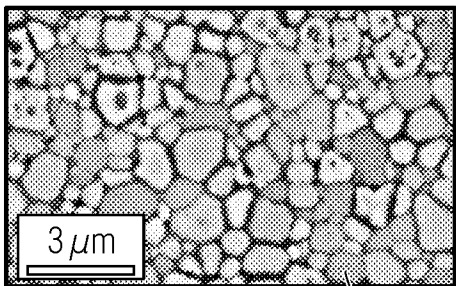


FIG. 24

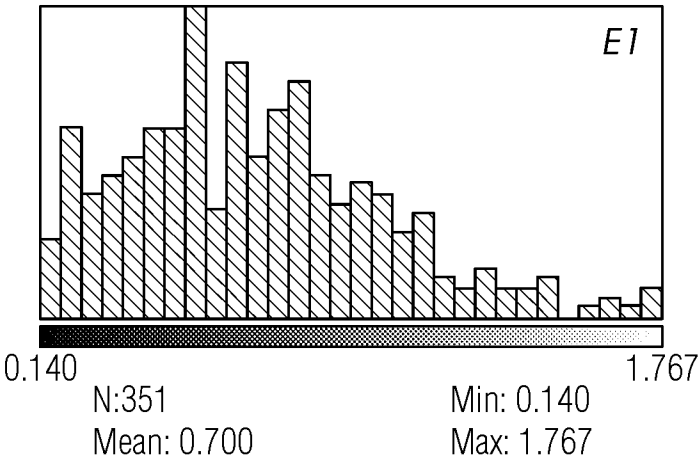


FIG. 25

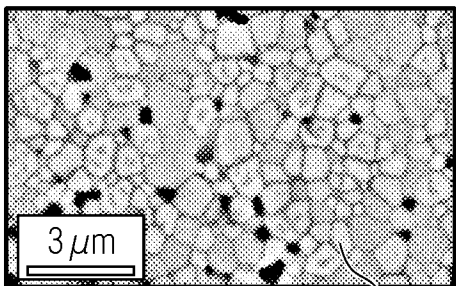


FIG. 26

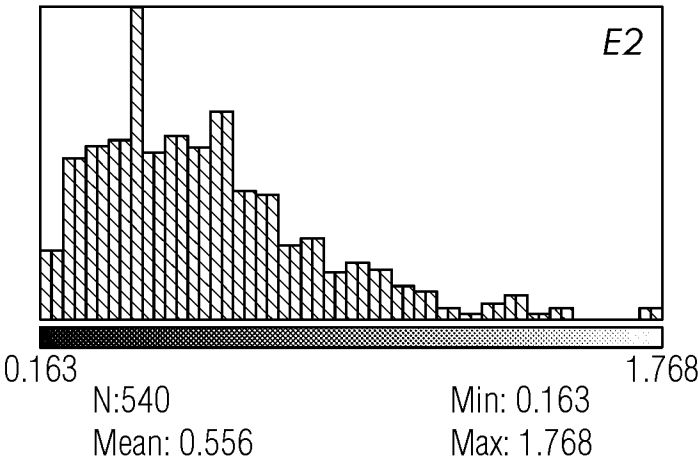


FIG. 27

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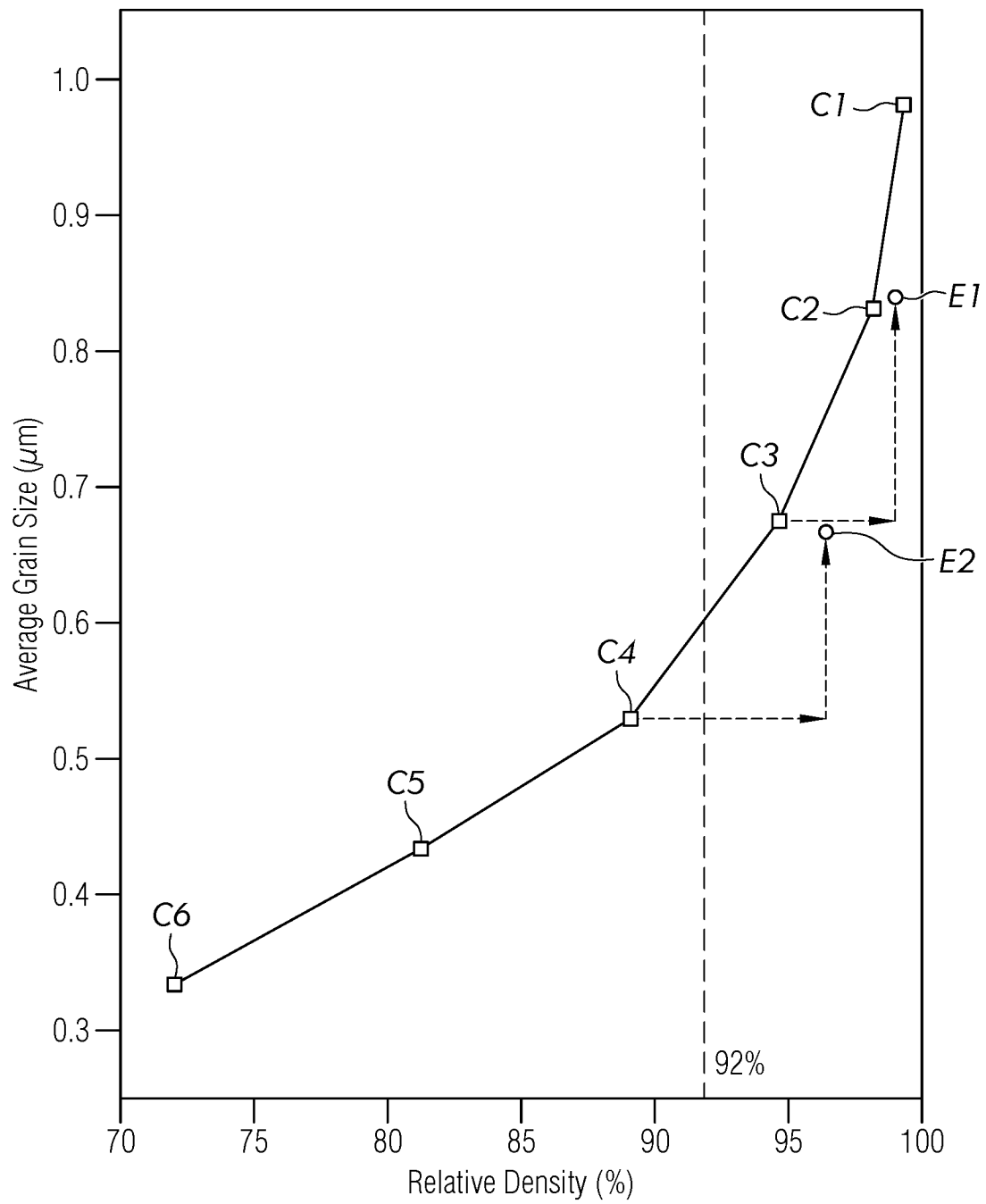


FIG. 28

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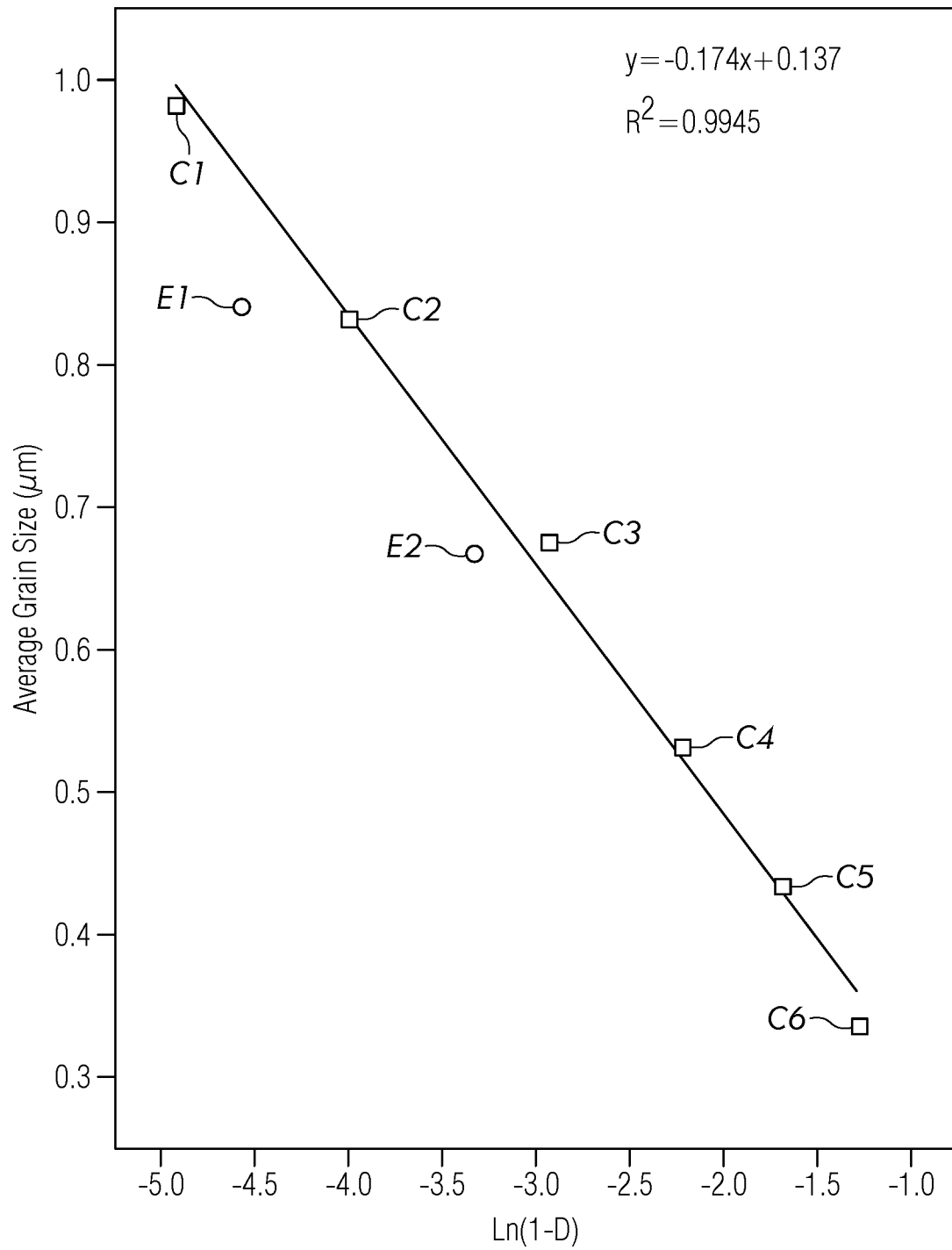


FIG. 29

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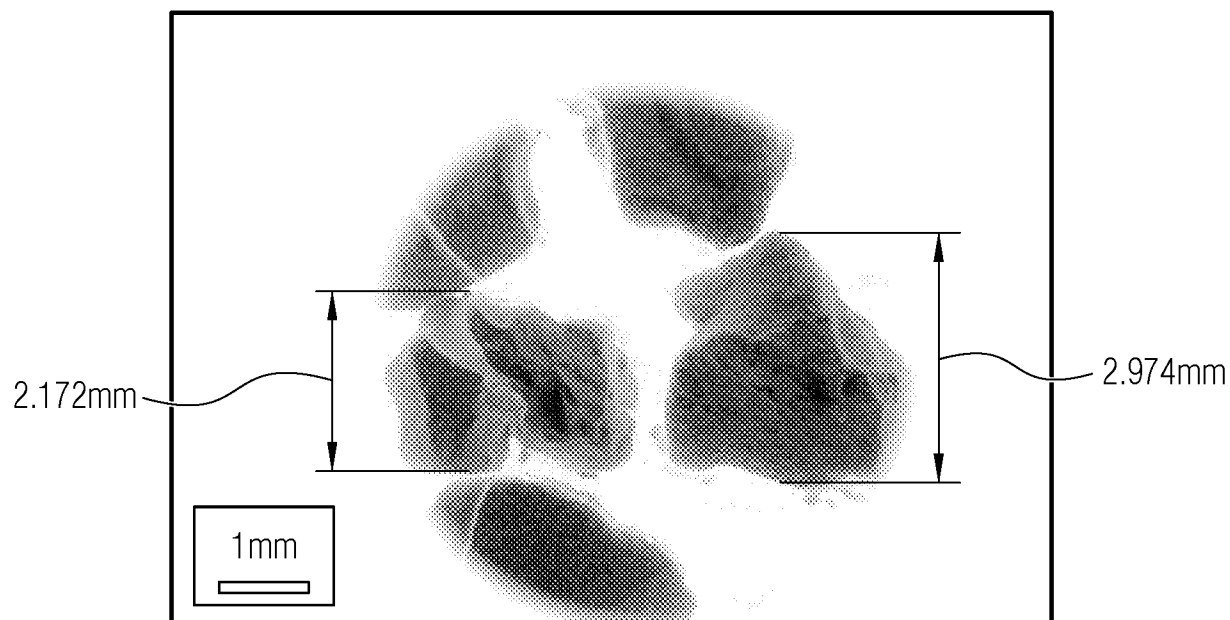


FIG. 30

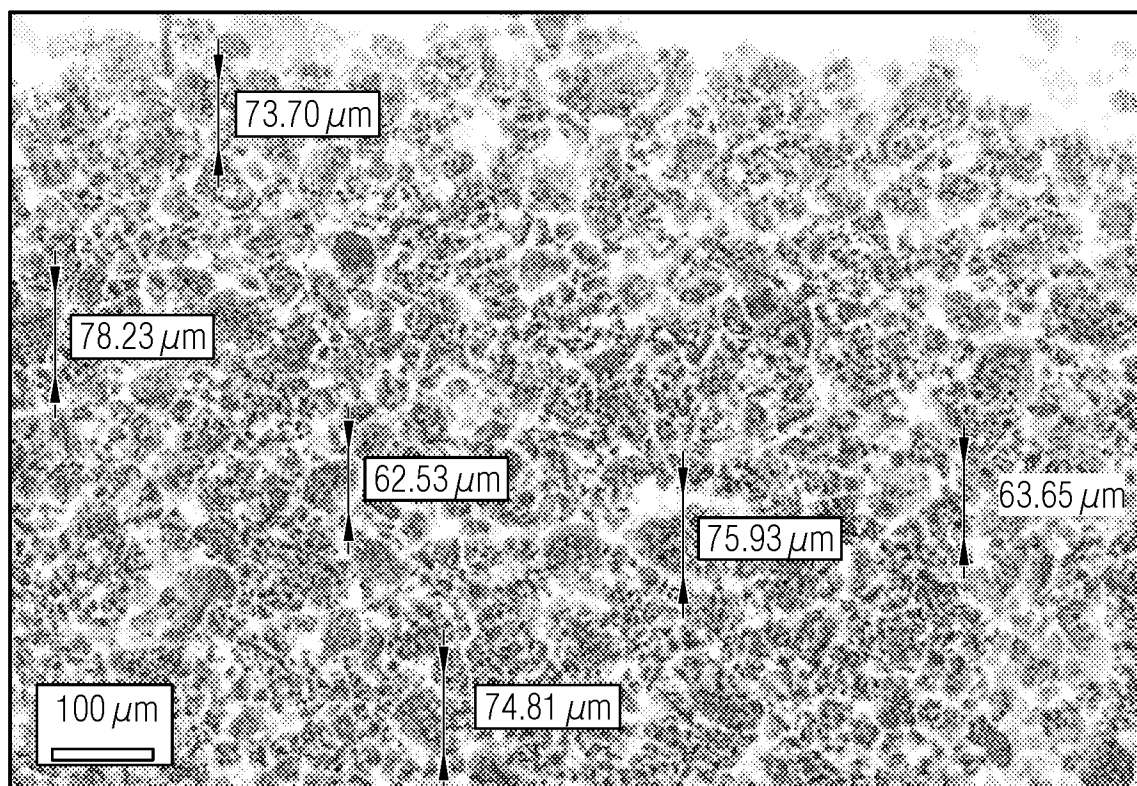


FIG. 31

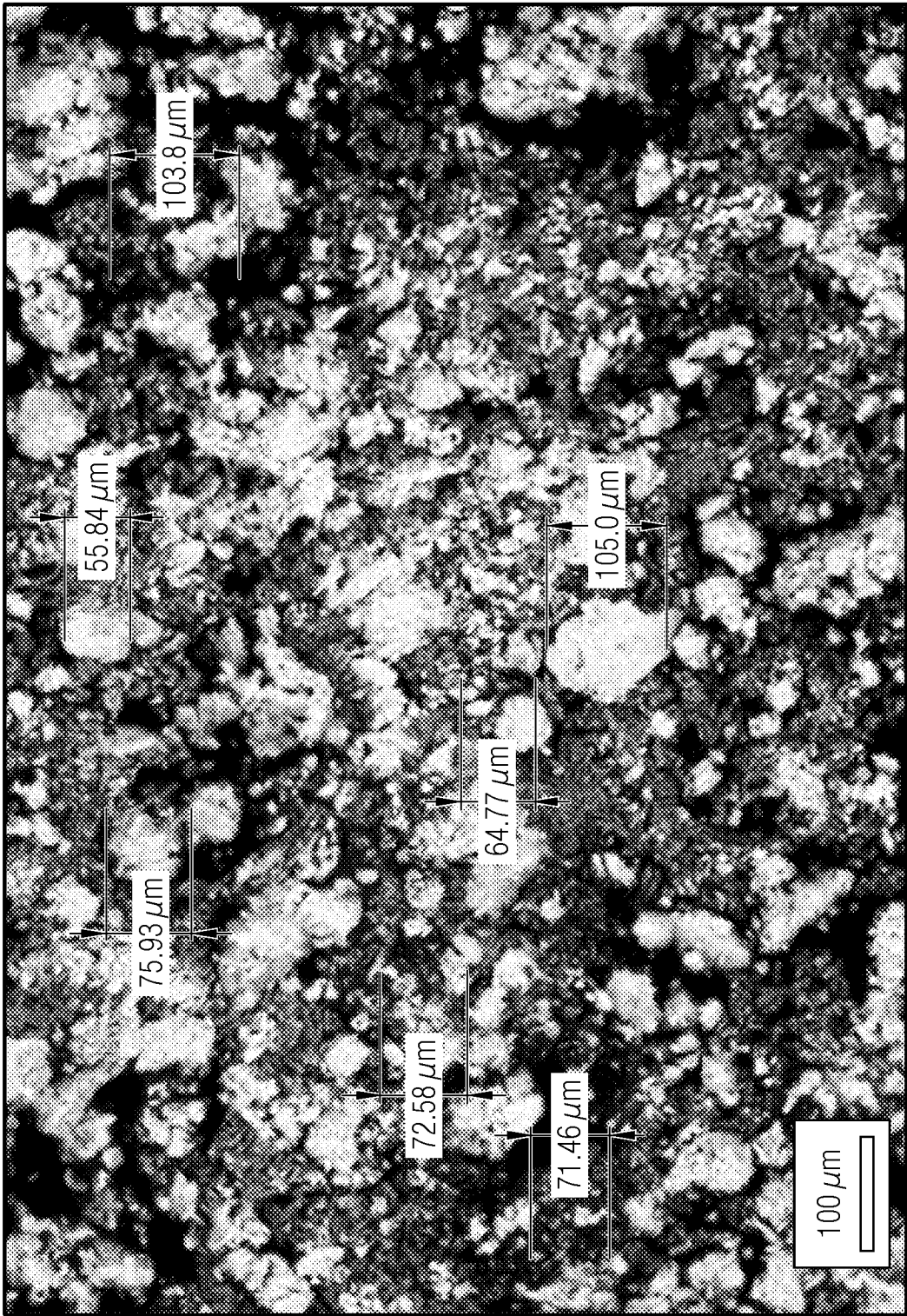


FIG. 32

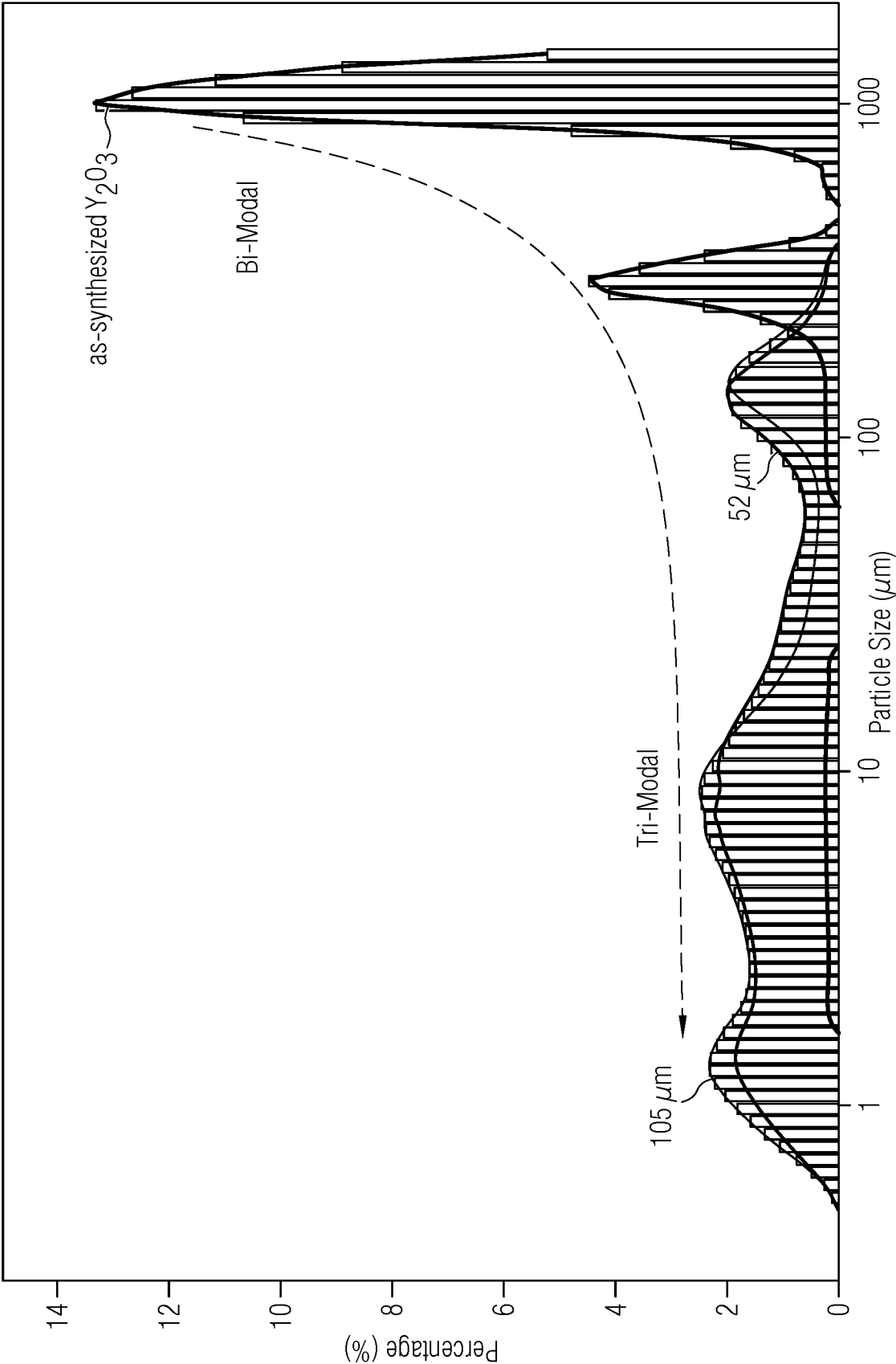
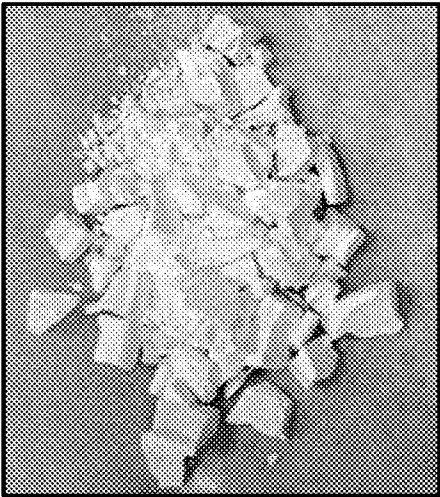
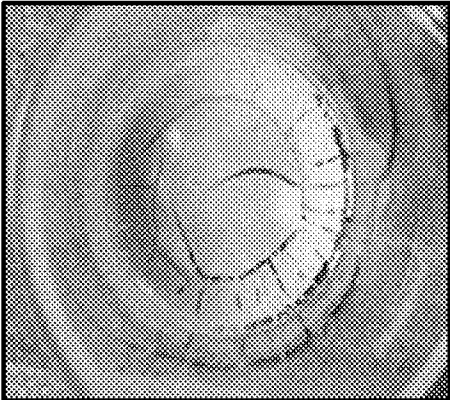


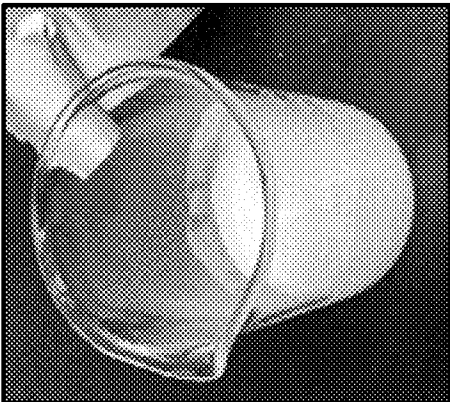
FIG. 33



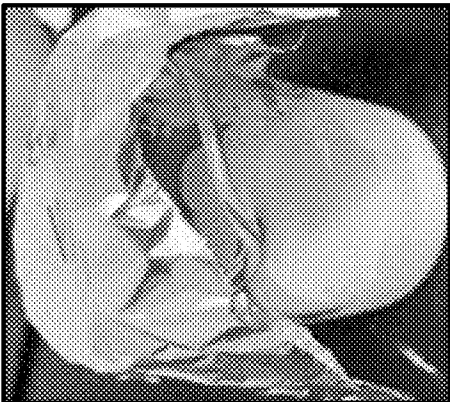
Day 5 - 7.7g



Day 4



Day 3



Day 0

FIG. 34

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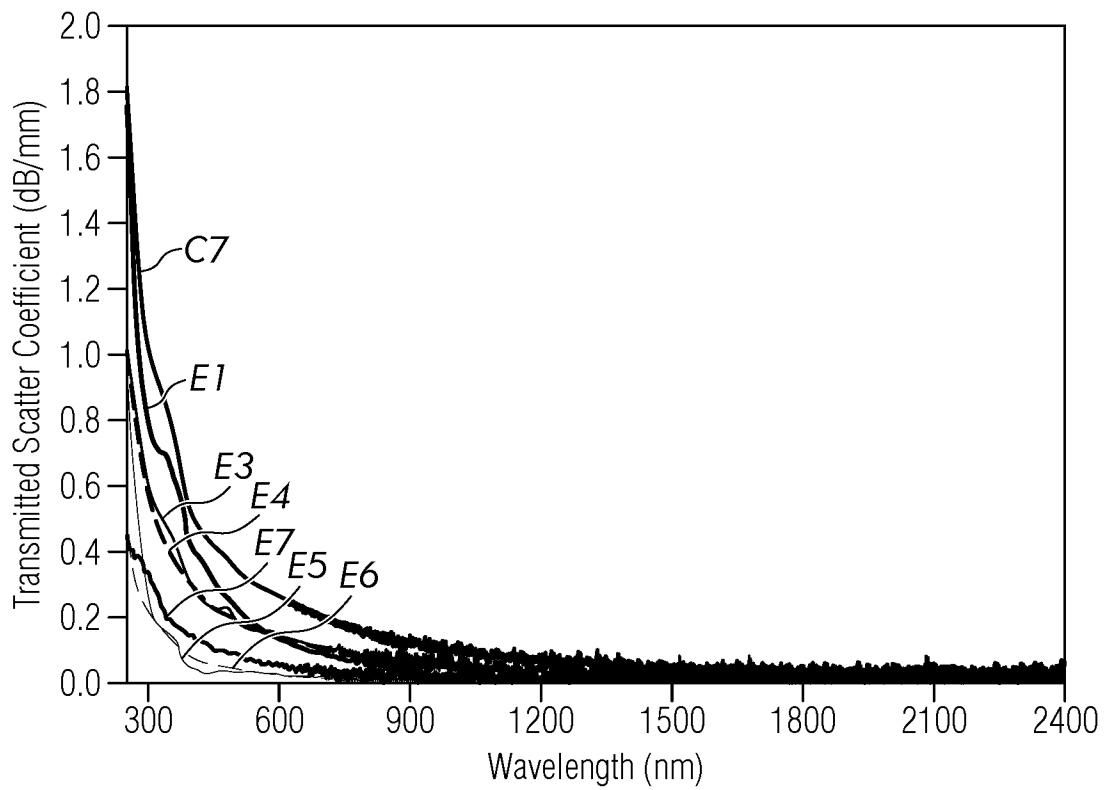


FIG. 35

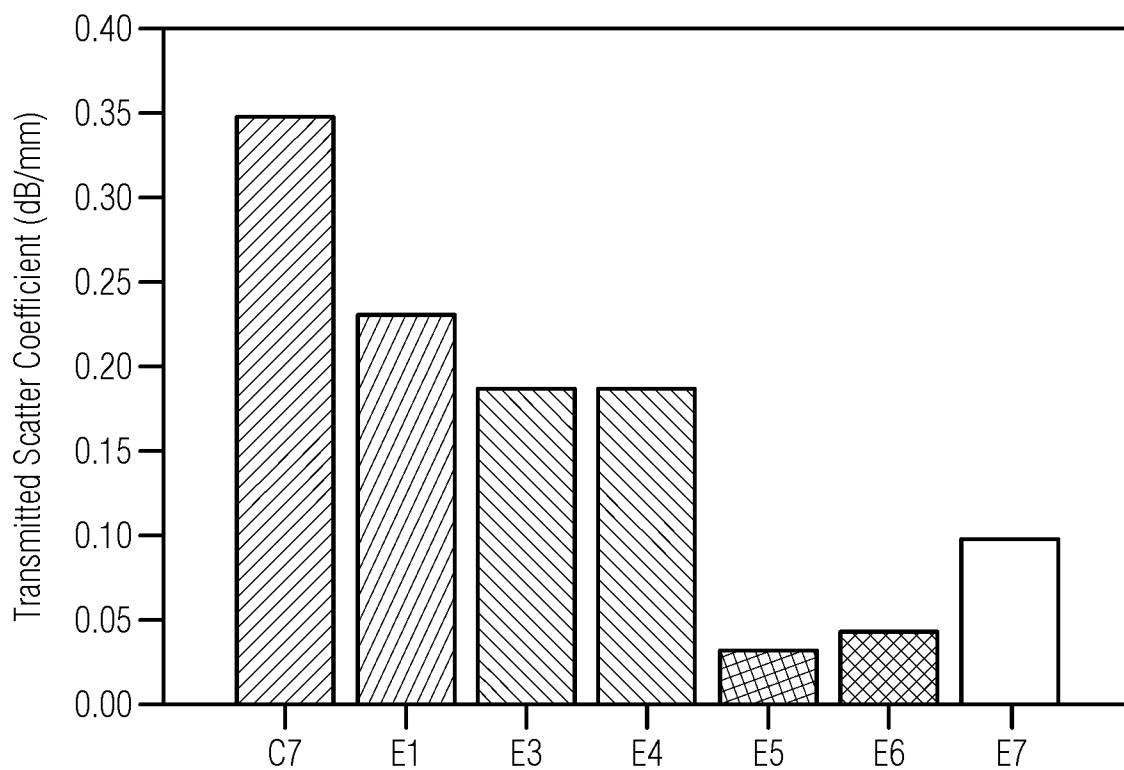


FIG. 36

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/056985

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C04B35/505 C04B35/626 C04B35/645

ADD.

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)

**C04B**

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

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

**EPO-Internal****C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                    | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 11 465 941 B2 (CORNING INC [US])<br>11 October 2022 (2022-10-11)<br>col.18, l. 32 - col. 19, l.11 & fig. 5<br>-----                                                                                                                                                                                                                                                                                                                                | 1 - 57                |
| X         | YANG JUN ET AL: "Er-doped Y2O3<br>transparent ceramic for quantum memory<br>applications",<br>PROCEEDINGS OF SPIE; [PROCEEDINGS OF SPIE;<br>ISSN 0277-786X; VOL. 8615], SPIE, 1000<br>20TH ST. BELLINGHAM WA 98225-6705 USA,<br>vol. 10771, 18 September 2018 (2018-09-18)<br>, pages 1077109-1077109, XP060113020,<br>DOI: 10.1117/12.2320693<br>ISBN: 978-1-5106-2099-5<br>3.2 Transparent Er3+ doped Y2O3 Ceramics;<br>table 1<br>-----<br>- / - - | 1 - 57                |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

**4 February 2025**

Date of mailing of the international search report

**24/02/2025**

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

Authorized officer

**Munro, Brian**

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/056985

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                            |                                                        |
|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                         | Relevant to claim No.                                  |
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