sintering of thin films, these films tend to crack, warp, or otherwise have surface deteriorations.

[0005] There is therefore a series of problems in the relevant field related to casting green tapes of ceramics, such as but not limited to garnets, and to sintering these green tapes to prepare high density garnet thin films. What is needed in the relevant field is, for example, improved materials and processes for casting green tapes with high density.

SUMMARY

[0006] The instant disclosure sets forth such materials and processes, in addition to making and using the same, and other solutions to problems in the relevant field.

[0007] ~~In one embodiment,~~ There is provided a process for making a high density green tape is provided, the process comprising:

(a) providing a slurry comprising at least one source powder;
(b) mixing the slurry with a binder solution in a non-reactive environment;
(c) casting the slurry to form a green tape in a non-reactive environment; and
(d) drying the green tape in a non-reactive environment to achieve density >2.9 g/ml.

In certain ~~embodiments~~examples, each non-reactive environment is unique with regard to temperature, pressure, or atmosphere composition. In certain examples~~embodiments~~, each non-reactive environment is the same non-reactive environment.

[0007a] In one aspect, there is provided a process for making a high density green tape, the process comprising:

(a) providing a slurry comprising a source powder;
(b) mixing the slurry with a binder solution in a non-reactive environment;
(c) casting the slurry to form a green tape in a non-reactive environment; and
(d) drying the green tape in a non-reactive environment to achieve a geometric density greater than 2.9 g/ml,

wherein the non-reactive environment comprises nitrogen gas or argon gas, or a combination thereof, and a humidity at about -10°C to -20°C, at about -20°C to

-30°C, at about -30°C to -40°C, at about -40°C to -50°C, or at about -50°C to -60 °C dew point.

[0008] In some examples~~embodiments~~, the at least one source powder is calcined in a non-reactive environment to achieve density >4.7 g/ml as measured by geometric density. In some examples~~embodiments~~, the amount of the at least one source powder in the green tape is at least 50%, 55%, 55%, 60%, 65%, 70%, 80%, 85%, or 90% by weight. In some examples~~embodiments~~, the at least one source powder is selected from the group consisting of lithium-stuffed garnet, chemical precursors to lithium-stuffed garnet, and lithium-stuffed garnet with aluminum oxide dopants. In some examples~~embodiments~~, the lithium-stuffed garnet is a material selected from the group consisting of: $Li_ALa_BM'_cM''_DZr_EO_F$, wherein $4<A<8.5$, $1.5<B<4$, $0\leq C\leq 2$, $0\leq D\leq 2$; $0\leq E<2.5$, $10<F\leq 13.5$, and M' and M'' are each, independently in each instance selected from Al, Mo, W, Nb, Sb, Ca, Ba, Sr, Ce, Hf, Rb, Ga, and Ta. In some examples~~embodiments~~, the particle size d_{50} is about 100 nm-200 nm, about 200 nm-300 nm,

about 300 nm-400 nm, about 400 nm-500 nm, about 500 nm-600 nm, about 600 nm-700 nm, about 700 nm-800 nm, about 800 nm-900 nm, about 900 nm-1 μm, about 1 μm-2 μm, or about 2 μm-3 μm.

[0009] In some examples~~embodiments~~, the process further comprises milling the at least one source powder in a non-reactive environment in an anhydrous aprotic solvent. In some examples~~embodiments~~, the non-reactive environment comprises nitrogen gas and humidity at about -10°C to -20°C, at about -20°C to -30°C, at about -30°C to -40°C, at about -40°C to -50°C, or at about -50°C to -60 °C dew point. In some examples~~embodiments~~, the non-reactive environment comprises argon gas and humidity at about -10°C to -20°C, at about -20°C to -30°C, at about -30°C to -40°C, at about -40°C to -50°C, or at about -50°C to -60 °C dew point. In some examples~~embodiments~~, the aprotic solvent is selected from the group consisting of: benzene, toluene, xylene, ethyl acetate, tetrahydrofuran, dioxane, and 1,2-dimethoxyethane. In some examples~~embodiments~~, milling is selected from the group consisting of dry milling, attrition milling, sonication milling, high energy milling, wet milling, jet milling, and cryogenic milling. In some examples~~embodiments~~, the source powder is milled until it has a particle size d_{50} that is about 100 nm-200 nm, about 200 nm-300 nm, about 300 nm-400 nm, about 400 nm-500 nm, about 500 nm-600 nm, about 600 nm-700 nm, or about 700 nm-750nm.

[0010] In some examples~~embodiments~~, prior to step (c) or step (d), the process includes mixing the slurry of the modified source powder in a non-reactive environment with a binder selected from the group consisting of polypropylene (PP), atactic polypropylene (aPP), isotactic polypropylene (iPP), other polyolefins such as ethylene propylene rubber (EPR), ethylene pentene copolymer (EPC), polyisobutylene (PIB), styrene butadiene rubber (SBR), poly(ethylene-co-1-octene) (PE-co-PO), poly(ethylene-co-methylene cyclopentene) (PE-co-PMCP), stereoblock polypropylenes, polypropylene polymethyl pentene, polyethylene oxide (PEO), PEO block copolymers, silicone polymers and copolymers, polyvinyl butyral (PVB), poly(vinyl acetate) (PVAc), polyvinylpyrrolidine (PVP), poly(ethyl methacrylate) (PEMA), acrylic polymers (for example polyacrylates, polymethacrylates, and copolymers thereof), binders from the Paraloid family of resins, binders from the Butvar family of resins, binders from the Mowital family of resins, and combinations thereof. In some examples~~embodiments~~, milling the slurry of the modified source powder, with a dispersant selected from the group consisting of fish oil, fatty acids of degree C_8– C_{20}, alcohols of degree C_8– C_{20}, alkylamines of degree C_8– C_{20}, phosphate

esters, phospholipids, olymeric dispersants such as poly(vinylpyridine), poly(ethylene imine), poly(ethylene oxide) and ethers thereof, poly(ethylene glycol) and ethers thereof, polyalkylene amine, polyacrylates, polymethacrylates, poly(vinyl alcohol), poly(vinyl acetate), polyvinyl butyral, maleic anhydride copolymers, glycolic acid ethoxylate lauryl ether, glycolic acid ethoxylate oleyl ether, sodium dodecyl sulfate, sodium dodecylbenzenesulfonate, cetyltrimethylammonium bromide, cetylpyridinium chloride, surfactants and dispersants from the Brij family of surfactants, the Triton family of surfactants, the Solsperse family of dispersants, the SMA family of dispersants, the Tween family of surfactants, and the Span family of surfactants. In some examples~~embodiments~~, the fatty acids of degree C_8– C_{20} are at least one of dodecanoic acid, oleic acid, stearic acid, linolenic acid, and/or linoleic acid. As used herein, degree C_8-C_{20} means that the described organic group includes 8 to 20 carbon atoms. In some examples~~embodiments~~, the alcohols of degree C_8– C_{20} are at least one of dodecanol, oleyl alcohol, and/or stearyl alcohol. In some examples~~embodiments~~, the alkylamines of degree C_8– C_{20} are at least one of dodecylamine, oleylamine, and/or stearylamine. In some examples~~embodiments~~, the phospholipids are phosphatidylcholine and/or lecithin. In some examples~~embodiments~~, the process further comprises, prior to step (c) or step (d), mixing the slurry of the source powder in a non-reactive environment with a plasticizer selected from dibutyl phthalate, dioctylphthalate, and benzyl butyl phthalate. In some examples~~embodiments~~, the filtration technique is selected from the group consisting of sieving, centrifugation, and separating particles of different size or different mass. In some examples~~embodiments~~, the slurry has a solid loading of 1 wt% to 99 wt% and wherein the solid loading refers to the amount of source powder. In some examples~~embodiments~~, the slurry when dried comprises the source powder at 80% wt/wt. In some examples~~embodiments~~, the slurry when dried comprises about 10-25% wt/wt organic content and wherein the organic content comprises slurry components other than the source powder. In some examples~~embodiments~~, the green tape has a density above 2.9 g/cm^3 as measured by geometric density. In some examples~~embodiments~~, the green tape is sintered.

[0011] In some examples, including any of the foregoing, the filtration technique occurs in a non-reactive environment. In some examples, including any of the foregoing filtering, the process includes filtering the slurry in a non-reactive environment.

[0012] Some examples ~~embodiments~~ provide a free-standing green tape comprising

a. lithium-stuffed garnet particles or particles of precursors to lithium-stuffed garnet; and
b. at least one element selected from a binder, a plasticizer, a dispersant, and a surfactant.

[0013] In some examples~~embodiments~~, the free-standing green tape has a density of 2.9 – 5.0 g/cm^3, a thickness of 0.5-100 μm, and a lateral extent of 0.5 – 400 cm^2. In some examples~~embodiments~~, the particles have a d_{50} of about 0.1-0.2 μm, about 0.2-0.3 μm, about 0.3-0.4 μm, about 0.4-0.5 μm, about 0.5-0.6 μm, about 0.6-0.7 μm, about 0.7-0.8 μm, about 0.8-0.9 μm, about 0.9-1.0 μm, about 1.0-1.1 μm. In some examples~~embodiments~~, the free-standing green tape has a thickness between about 500 nm and about 100 μm. In some ~~embodiments~~examples, green tape area is at least 0.5 cm^2. In some examples~~embodiments~~, green tape thickness varies by less than 5% over a 10 cm^2 area. In some examples~~embodiments~~, the green tape has a ceramic loading of about 50 - 80 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 55 - 80 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2, a ceramic loading of about 55- 75 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2, a ceramic loading of about 50 - 75 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2 , a ceramic loading of about 55 - 70 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2, a ceramic loading of about 50 - 65 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2, or a ceramic loading of about 55- 65 vol%, a thickness of about 0.5-100 μm, and a lateral extent of about 0.5 – 400 cm^2.

[0014] In some examples~~embodiments~~, including any of the foregoing, the green tape has a density of 2.9 – 5.0 g/cm^3, a thickness of 0.5-100um, and a lateral extent of 0.5 – 400 cm^2. In some examples~~embodiments~~, the particles have a d_{50} of about 0.1 - about 0.2 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.2 - about 0.3 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.3 - about 0.4 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.4 - about 0.5 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.5 - about 0.6 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.6 - about 0.7 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.7 - about 0.8 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.8 - about 0.9 μm. In some examples~~embodiments~~, the particles have a d_{50} of 0.9 - about 1.0 μm. In some examples~~embodiments~~, the particles have a d_{50} of or 1.0 - about 1.1 μm. In some examples~~embodiments~~, the free-standing green tape has a thickness between about 500 nm

and about 100 μm. In some examples~~embodiments~~, the green tape area is at least 0.5 cm^2. In some examples~~embodiments~~, the green tape thickness varies by less than 5% over a 10 cm^2 area. In some examples~~embodiments~~, the green tape has a source powder solid loading of about 50 - about 80 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 55 - about 80 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 55 - about 75 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 50 - about 75 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 55 - about 70 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 50 - about 65 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2. In some examples~~embodiments~~, the green tape has a ceramic loading of about 55 - about 65 vol%, a thickness of about 0.5 - about 100um, and a lateral extent of about 0.5 – 400 cm^2.

BRIEF DESCRIPTIONS OF THE DRAWINGS

[0015] Figure 1 shows an example flow chart in accordance with an embodiment of the process set forth herein.

[0016] Figure 2 shows a scanning electron microscopy (SEM) image of a green tape made by the casting process set forth in Example 1. The organic portion is labeled **201**, and the lithium-stuffed garnet portion is labeled **202**.

[0017] Figure 3 shows a scanning electron microscopy (SEM) image of a sintered green tape made by Example 1. The organic portion is labeled **301**, and the garnet portion is labeled **302**.

[0018] Figure 4 shows optical microscope images of a disc of green tape made by Example 1 before sintering, and the resulting disc obtained after sintering. The green tape disc is labeled **401**, and the sintered disc is labeled **402**.

CLAIMS

What is claimed is:

1. A process for making a high density green tape, the process comprising:

   (a) providing a slurry comprising a source powder;

   (b) mixing the slurry with a binder solution in a non-reactive environment;

   (c) casting the slurry to form a green tape in a non-reactive environment; and

   (d) drying the green tape in a non-reactive environment to achieve a geometric density greater than 2.9 g/ml,

   wherein the non-reactive environment comprises nitrogen gas or argon gas, or a combination thereof, and a humidity at about -10°C to -20°C, at about -20°C to -30°C, at about -30°C to -40°C, at about -40°C to -50°C, or at about -50°C to -60 °C dew point.

2. The process of claim 1, wherein the source powder is calcined in a non-reactive environment to achieve geometric density greater than 4.7 g/ml.

3. The process of claim 1, wherein the amount of source powder in the green tape is at least 50%, 55%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, or 90% by weight.

4. The process of any one of claims 1 to 3, wherein the at least one source powder is selected from the group consisting of lithium-stuffed garnet, chemical precursors to lithium-stuffed garnet, and lithium-stuffed garnet with aluminum oxide dopants.

5. The process of claim 4, wherein the lithium-stuffed garnet is a material selected from the group consisting of: $Li_ALa_BM'_cM''_DZr_EO_F$, wherein $4<A<8.5$, $1.5<B<4$, $0\leq C\leq 2$, $0\leq D\leq 2$; $0\leq E<2.5$, $10<F\leq 13.5$, and M' and M'' are each, independently in each instance selected from Al, Mo, W, Nb, Sb, Ca, Ba, Sr, Ce, Hf, Rb, Ga, and Ta.

6. The process of any one of claims 1 to 5, wherein at least one source has a particle size distribution d_{50} of about 100 nm - about 200 nm, about 200 nm - about 300 nm,

about 300 nm - about 400 nm, about 400 nm - about 500 nm, about 500 nm - about 600 nm, about 600 nm - about 700 nm, about 700 nm - about 800 nm, about 800 nm - about 900 nm, about 900 nm - about 1 μm, about 1 μm - about 2 μm, or about 2 μm - about 3 μm.

7. The process of any one of claims 1 to 6, wherein the process further comprises milling at least one source powder in a non-reactive environment in an anhydrous aprotic solvent.

~~8. The process of any one of claims 1 to 7, wherein the non-reactive environment comprises nitrogen gas or argon gas, or a combination thereof, and a humidity at about -10°C to -20°C, at about -20°C to -30°C, at about -30°C to -40°C, at about -40°C to -50°C, or at about -50°C to -60 °C dew point.~~

~~9. The process of any one of claims 7 to 8, wherein the aprotic solvent is selected from the group consisting of: benzene, toluene, xylene, ethyl acetate, tetrahydrofuran, dioxane, and 1,2-dimethoxyethane.~~

~~10. The process of any of claims 1-9, wherein the milling is selected from the group consisting of dry milling, attrition milling, sonication milling, high energy milling, wet milling, jet milling, and cryogenic milling.~~

~~11.~~8. The process of any one of claims 1-~~10~~7, further comprising milling the source powder until the source powder has a particle size distribution d_{50} of about 100 nm-200 nm, about 200 nm-300 nm, about 300 nm-400 nm, about 400 nm-500 nm, about 500 nm-600 nm, about 600 nm-700 nm, or about 700 nm-750nm.

~~12.~~9. The process of any one of claims 1 to ~~11~~8, further comprising, prior to step (c) or step (d), mixing the slurry of the modified source powder in a non-reactive environment with a binder selected from the group consisting of polypropylene (PP), atactic polypropylene (aPP), isotactic polypropylene (iPP), ethylene propylene rubber (EPR), ethylene pentene copolymer (EPC), polyisobutylene (PIB), styrene butadiene rubber (SBR), poly(ethylene-co-1-octene) (PE-co-PO), poly(ethylene-co-

methylene cyclopentene) (PE-co-PMCP), stereoblock polypropylenes, polypropylene polymethyl pentene, polyethylene oxide (PEO), PEO block copolymers, silicone polymers and copolymers, polyvinyl butyral (PVB), poly(vinyl acetate) (PVAc), polyvinylpyrrolidine (PVP), poly(ethyl methacrylate) (PEMA), acrylic polymers, binders from the Paraloid family of resins, binders from the Butvar family of resins, binders from the Mowital family of resins, and combinations thereof.

~~13.~~10. The process of any one of claims 1 to ~~12~~9, further comprising, in step (b), milling the slurry of the modified source powder, with a dispersant selected from the group consisting of fish oil, fatty acids of degree C_8– C_{20}, alcohols of degree C_8– C_{20}, alkylamines of degree C_8– C_{20}, phosphate esters, phospholipids, polymeric dispersants such as poly(vinylpyridine), poly(ethylene imine), poly(ethylene oxide) and ethers thereof, poly(ethylene glycol) and ethers thereof, polyalkylene amine, polyacrylates, polymethacrylates, poly(vinyl alcohol), poly(vinyl acetate), polyvinyl butyral, maleic anhydride copolymers, glycolic acid ethoxylate lauryl ether, glycolic acid ethoxylate oleyl ether, sodium dodecyl sulfate, sodium dodecylbenzenesulfonate, cetyltrimethylammonium bromide, cetylpyridinium chloride, surfactants and dispersants from the Brij family of surfactants, the Triton family of surfactants, the Solsperse family of dispersants, the SMA family of dispersants, the Tween family of surfactants, and the Span family of surfactants.

~~14.~~11. The process of claim ~~13~~10, wherein the fatty acids of degree C_8– C_{20} are selected from dodecanoic acid, oleic acid, stearic acid, linolenic acid, and/or linoleic acid.

~~15.~~12. The process claim 10~~13~~, wherein the alcohols of degree C_8– C_{20} are at selected from dodecanol, oleyl alcohol, stearyl alcohol, and combinations thereof.

~~16.~~13. The process of claim 10~~13~~, wherein the alkylamines of degree C_8– C_{20} are selected from dodecylamine, oleylamine, stearylamine, and combinations thereof.

~~17.~~14. The process of claim 10~~13~~, wherein the phospholipids are selected from phosphatidylcholine, lecithin, and combinations thereof.

~~18.~~15. The process of any one of claims 1 to ~~17~~14, further comprising, prior to step (c) or step (d), mixing the slurry of the source powder in a non-reactive environment with a plasticizer selected from dibutyl phthalate, dioctyl phthalate, and benzyl butyl phthalate.

~~19. The process of any one of claims 1 to 18, wherein the filtration technique is selected from the group consisting of sieving, centrifugation, and separating particles of different size or different mass.~~

~~20.~~16. The process of any one of claims 1 to ~~19~~15, wherein the slurry has a solids loading of 1 wt% to 99 wt% and wherein the solid loading refers to the amount of source powder.

~~21.~~17. The process of any one of claims 1 to ~~20~~16, wherein the slurry when dried comprises the source powder at 80% wt/wt.

~~22.~~18. The process of any one of claim 1 to ~~21~~17, wherein the slurry when dried comprises about 10-25% wt/wt organic content and wherein the organic content comprises slurry components other than the source powder.

~~23.~~19. The process of any one of claim 1 to ~~22~~18, wherein the green tape comprises particles of a lithium-stuffed garnet, or wherein the green tape has a density greater than 2.9 g/cm^3 as measured by geometric density.

~~24. The process of any one of claim 1 to 23, wherein the green tape has a density greater than 2.9 g/cm^3 as measured by geometric density.~~

~~25. The process of any one of claims 1-24, further comprising sintering the green tape.~~

~~26. The process of any one of claims 1 to 7, wherein the non-reactive environment comprises atmospheric air at a humidity of about -10°C to -20°C, at about -20°C to -30°C, at about -30°C to -40°C, at about -40°C to -50°C, or at about -50°C to -60 °C dew point.~~

~~27. The process of any one of claims 1-26, wherein the non-reactive environment is the same non-reactive environment in each step.~~

~~28. The process of any one of claims 1-26, wherein the non-reactive environment is a different non-reactive environment in at least one step.~~