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(54) Title: SYNTHESIS OF M13 CLUSTERS FROM ALUMINUM AND GALLIUM MINERAL POLYMORPHS

(57) Abstract: A method comprising reacting an aluminum mineral polymorph or a gallium mineral polymorph with an acid at an aluminum metal to acid molar ratio or gallium metal to acid molar ratio sufficient to produce M_{13} nanoscale clusters, M nano- agglomerates, or a M_{13} slurry, wherein M is Al or Ga.

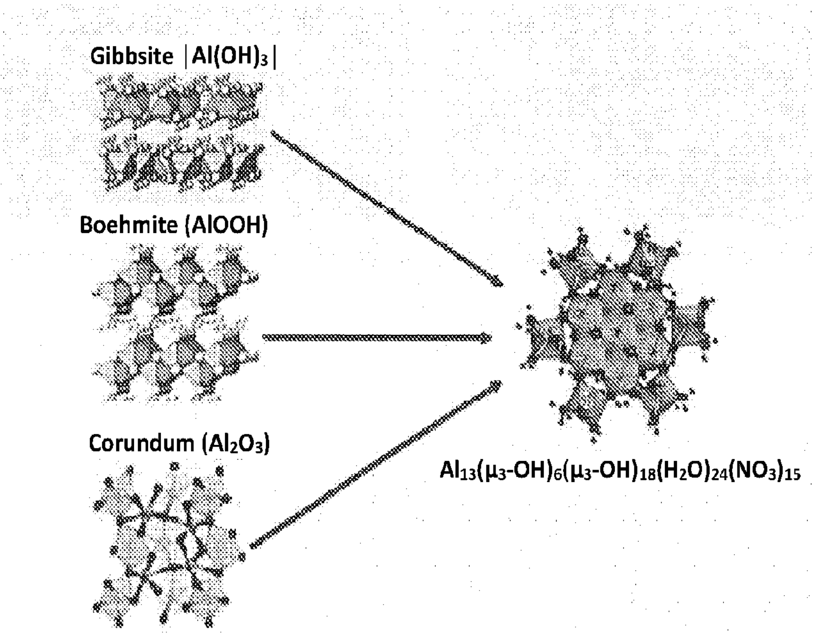

FIG. 1

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SYNTHESIS OF M_{13} CLUSTERS FROM ALUMINUM AND GALLIUM MINERAL POLYMORPHS

This application claims the benefit of U.S. Provisional Application No. 62/190,676, filed July 9, 2015, which is incorporated herein by reference.

BACKGROUND

Metal oxide (M_xO_y) semiconducting materials have had a profound impact on the market for thin film device applications for numerous years. However, cost-effective mass production of high-purity materials remains challenging for scientists and engineers.

SUMMARY

Disclosed herein is a method comprising:

reacting an aluminum mineral polymorph or a gallium mineral polymorph with an acid at an aluminum metal to acid molar ratio or gallium metal to acid molar ratio sufficient to produce M_{13} nanoscale clusters, M nano-agglomerates, or a M_{13} slurry, wherein M is Al or Ga.

Also disclosed herein is a method comprising:

mixing an aluminum mineral polymorph or a gallium mineral polymorph with an acid to produce a slurry; and

processing the slurry under conditions sufficient to produce an aqueous solution of $M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ nanoscale clusters, wherein M is Al or Ga.

The foregoing will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a structural representation of various aluminum materials that were converted to flat-Al_{13} clusters via acidification according to the methods disclosed herein.

FIG. 2 shows overall balanced equations for the reaction of metal bulk materials and HNO_3.

FIGS. 3A and 3B are optical microscope images of Al_{13} (FIG. 3A) and Ga_{13} (FIG. 3B) single crystal produced from the acidification process disclosed herein.

FIGS. 4A and 4B show dynamic light scattering of Al_{13} (FIG. 4A) and Ga_{13} (FIG. 4B) in 0.1 M aqueous solutions.

FIGS. 5A and 5B are solid state Raman spectra of Al_{13} (FIG. 5A) and Ga_{13} (FIG. 5B). Both spectra are consistent with previous reports of both clusters.

FIG. 6 is a powder x-ray of Al_{13} experimental compared with literature references.

FIG. 7 is a ^{27}Al NMR spectra of Al13 Keggin ions from different synthetic methods.

FIG. 8 is a graph showing dielectric constants for Al_2O_3 thin-films from precursors disclosed herein with selected ratios of NO_3^-:Al^{3+}. The Keggin ion (Ratio 0.5 NO_3^-:1 Al^{3+}) shows a higher dielectric constant, suggesting that the material makes more continuous (less porous) thin-films with a 350 °C anneal. The inset shows the test structure of the MIS device used for the CV measurement.

DETAILED DESCRIPTION

Methods such as vapor deposition are effective for producing atomically-uniform metal oxide thin films; however the process is expensive, time consuming, and product yields are low. Although solution processing of $M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ (M = Al or Ga) clusters is potentially a viable alternative to traditional deposition methods, product variability, reaction conditions, and long reaction times are deterrents for large-scale production. Advancements in the understanding of cluster reactivity have allowed chemists to develop more efficient and safer methods that utilize reducing agents such as zinc and electrochemical titrations to produce the aforementioned clusters. These methods however have significant drawbacks that include: long crystallization periods, extensive purification requirements, production of toxic byproducts, and the use of non-trivial and often expensive electrochemical apparatuses.

Disclosed herein is a facile and non-toxic synthesis of M_{13} clusters. For convenience, "M_{13} clusters" refers to $[M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]_a[X]_{15a}$, wherein a is an integer of 1 to 4, $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$, wherein b is an integer of 1 to 4, or a mixture thereof, wherein M is Al or Ga and X is a counterion derived from a protic acid. In certain embodiments, a M_{13} cluster is $M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$. $[M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]_a[X]_{15a}$ is also known as “flat” M_{13} and $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$ is also known as “Keggin” M_{13}. “M nano-agglomerates” refers to a composition comprising M_y species, wherein y is 2 to 32. For example, M nano-agglomerates may include M_{13} clusters and at least one further M-containing component such as, for example, M-containing dimers and/or trimers, and/or larger aggregates such as M_{26}, M_{30}, or M_{32}. This synthesis requires no purification and takes advantage of acid-base chemistry to produce scalable quantities of clusters, nano-agglomerates, and slurries in high quantitative yields.

In one embodiment, a simple, inexpensive, and atom economical method has been developed to synthesize aqueous flat M_{13} or Keggin M_{13} nanoclusters via acidification of representative mineral polymorphs of purified aluminum or gallium oxides, oxyhydroxides, and/or hydroxides (M_2O_3, MO(OH), or $M(OH)_3$ where M = Al or Ga).

Under this principle, the acidification can be done directly with the mineral mined directly from the Earth, but would most likely require some form of purification and separation of other agglomerate material that may be present. With this synthetic route, these clusters can be produced on a mass scale and be potentially utilized for solution processing of amorphous metal oxide (M_2O_3) dielectric thin film devices commercially. Additionally, the slurry mixture can be used as a polishing agent for surface smoothing.

Nanoscale clusters generally refers to discrete, monodispersed architectures of oligomers linked together with defined dimensions that range from $1 \text{ nm} \leq x \text{ nm} < 5 \text{ nm}$, while nano-agglomerate species refer to dimensions ranging from $5 \text{ nm} \leq x \text{ nm} < 200 \text{ nm}$, and slurries are insoluble motifs that are 200 nm and beyond.

Aqueous nanoscale clusters, nano-agglomerates, and slurry mixtures have been synthesized via the acidification of bulk aluminum and gallium minerals/materials. This process can be carried out at wide concentration gradients from, for example, 1 mM to 4 M metal content and requires virtually no post-reaction purification or separation of excess monomer formed or initial reactant material used. The acidification products have a hydrodynamic radii of 1 nm ± 0.1 nm and can then be used directly “as is” as solution precursors for thin film fabrication so long as the original products used are pure (see, e.g., U.S. Patent No. 9,340,678, for a description of the use as precursors for thin film fabrication). This synthetic route represents a facile, economical, and scalable scheme to mass-produce desirable precursor materials for solution processing transparent thin film devices. Identification of these clusters in the solid and solution states with powder x-ray diffraction, optical microscopy, Raman spectroscopy, and dynamic light scattering was consistent with data previously reported in the literature.

More specifically, disclosed herein in certain embodiments are methods for reacting an aluminum containing polymorphs or a gallium containing polymorphs with an acid to produce M_{13} nanoscale clusters (e.g., $M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}(NO_3)_{15}$ nanoscale clusters). Also disclosed herein are methods of mixing an aluminum containing polymorph or a gallium containing polymorph mineral with an acid to produce a slurry, and processing the slurry under high enough acidic conditions (metal to acid ratio > 1:0.7 mol. eq.) sufficient to produce an aqueous solution of M_{13} nanoscale clusters (e.g., $M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}(NO_3)_{15}$ nanoscale clusters).

In principle, any representative mineral polymorph regardless of oxidation state can be made into a slurry or solution nanoscale cluster or nanoagglomerate in solution under the following conditions: the final product of cluster or agglomerate must contain a stabilizing proton accepting ion [ex. NO_3^-, PO_4^{3-}, ClO_4^-, SO_4^{2-}, (X^- where X = F, Cl, Br, or I), CO_3^{2-}, TsO^-, MnO_4^-, SeO_4^{2-}] that would be generated via use of their corresponding acids, stable in the solid state and insoluble from a pH gradient of weakly acidic to weakly basic, and exhibits amphoterism. Thus X in $[M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}]_a[X]_{15a}$ or $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$ may be monovalent counterion (meaning that subscript a or b is 1) or a polyvalent counterion (meaning that subscript a or b is greater than 1).

Illustrative aluminum-containing mineral polymorphs include corundum, gibbsite, boehmite, diaspore, bayerite, and nordstrandite and any combination or mixture thereof. Illustrative gallium-containing mineral polymorphs include $Ga(O)OH$, Ga_2O_3, $Ga(OH)_3$ (sohngeite), and any combination or mixture thereof. The acid may be any acid that dissolves the mineral. Illustrative acids that have the ability to dissolve the material include nitric acid, sulfuric acid, selenic acid, halide acids (e.g., hydrochloric acid, hydrobromic acid, hydroiodic acid, chloric acid, bromic acid, iodic acid), sulfonic acids (e.g., tosylic acid, sulfanilic acid, benzene sulfonic acid, salicylic acid, Armstrong's acid, triflic acid), carboxylic acids (formic acid, oxalic acid, acetic acid, carbonic acid), and a mixture thereof. Nitric acid is a preferred acid 1:0.3 – 1:0.65 mol. eq. of metal to acid ratio to produce slurries and 1:0.7 – 1:1.15 mol eq. of metal to acid ratio to produce nanoagglomerates, and 1:1.15 – 1:1.3 mol eq. of metal to acid to produce clusters). All other monovalent acids listed above will follow the same stoichiometry as nitric acid.

In certain embodiments, 1:1.15 – 1:1.3 mol eq. of metal to acid ratio will produce flat $[M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}]_a[X]_{15a}$. Of note, $[M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}]_a[X]_{15}$ clusters wherein X is polyvalent counterion (e.g., a divalent counterion such as SO_4^{2-}) can be produced by the methods disclosed herein.

In certain embodiments, 1:0.3 – 0.65 mol. eq. of metal to acid ratio (more particularly 1:0.45 – 0.65) will produce Keggin $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$. Of note, $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$ clusters wherein X is a monovalent counterion (e.g., NO_3^-) can be produced by the methods disclosed herein.

The mineral polymorph (M) is reacted with the acid, for example, at a M^{3+}:NO_3^- molar ratio in a range to produce nanoscale clusters. In certain embodiments, the M^{3+}:NO_3^- molar ratio is tunable over a wide concentration gradient, provided the M^{3+}:NO_3^- molar ratio is controlled via controlling the mol. eq. of metal to acid so that the reaction does not proceed to formation of the metal nitrate salt (e.g., $Al(NO_3)_3$ or gallium nitrate $Ga(NO_3)_3$). Overall balanced equations for the reaction of metal bulk materials and HNO_3 are shown in FIG. 1. The reaction parameters and overall balanced equations are also applicable to acids other than nitric acid.

The mixing typically is carried out until complete dissolution occurs, causing a clear solution.

The slurry may be mixed at temperatures ranging from 25 to 100 °C, more particularly 45 to 80 °C, and most particularly 55 to 75 °C.

The methods described herein may have a reaction time of 12 to 72 hours, more particularly 24 to 36 hours.

The methods disclosed herein do not require the use of any secondary reagents to facilitate cluster formation (e.g., zinc powder or di-butyl nitrosamine) or a potentially expensive electrochemical apparatus setup.

The methods disclosed herein can produce M_{13} nanoscale clusters on a mass scale since the methods are very amenable to scaling up. For example, different forms of aluminum and gallium minerals can be used as starting materials under the same reaction conditions while consistently achieving the same M_{13} end product. Only simple, inexpensive, and readily available reagents are used and can be readily scaled up to at least the kilogram scale. Atom economy for these methods is upwards of 90% yield, with water being the primary byproduct.

The methods disclosed herein may result in the formation of an M_{13} nano-aggregate solution that has several different uses. For example, the M_{13} nano-aggregate solution may be used as industrial polishing agent for chemical-mechanical planarization (CMP). In a further example, the M_{13} nano-aggregate solution may be used as solution precursors for solution processing of metal oxide (M_2O_3) thin films for electronic device. For instance, transparent conductive oxide materials containing Al^{3+} and/or Ga^{3+} species derived from the aqueous precursors disclosed herein may be made.

Certain illustrative embodiments are described in consecutively numbered clauses as shown below:

1. A method comprising:

reacting an aluminum mineral polymorph or a gallium mineral polymorph with an acid at an aluminum metal to acid molar ratio or gallium metal to acid molar ratio sufficient to produce $M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}(NO_3)_{15}$ nanoscale clusters, nano-agglomerates, or a slurry, wherein M is Al or Ga.

2. A method comprising:

mixing an aluminum mineral polymorph or a gallium mineral polymorph with an acid to produce a slurry; and

processing the slurry under conditions sufficient to produce an aqueous solution of $M_{13}(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{18}(H_2O)_{24}(NO_3)_{15}$ nanoscale clusters, wherein M is Al or Ga.

3. The method of clause 1 or 2, wherein the aluminum mineral polymorph is selected from corundum, gibbsite, boehmite, diaspore, bayerite, nordstrandite, or any combination or mixture thereof.

4. The method of clause 1 or 2, wherein the gallium mineral polymorph is selected from Ga(O)OH, Ga_2O_3, $Ga(OH)_3$, or any combination or mixture thereof.

5. The method of any one of clauses 1 to 4, wherein the acid is selected from nitric acid, sulfuric acid, selenic acid, a halide acid, a sulfonic acid, a carboxylic acid, or a mixture thereof.

6. The method of any of clauses 1 to 4, wherein the acid is nitric acid.

7. The method of any one of clauses 1 or 3 to 6, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:0.3 mol eq of metal to acid to 1:1.3 mol. eq. of metal to acid.

8. The method of any of clauses 2 to 6, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is greater than 1:0.7 mol eq.

9. The method of clause 6, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:0.3 to 1:0.65 mol eq to produce the slurry.

10. The method of clause 6, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:0.7 to 1:1.0 mol eq to produce the nano-agglomerates.

11. The method of clause 6, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:1.15 to 1:1.3 mol eq to produce the nanoscale clusters.

12. The method of any one of clauses 1 to 11, wherein the method is controlled to avoid formation of $Al(NO_3)_3$ or $Ga(NO_3)_3$.

13. The method of any one of clauses 1 to 12, wherein the nanoscale clusters have a dimension ranging from 1 nm to 5 nm.

14. The method of any one of clauses 1 or 3 to 12, wherein the nano-agglomerates have a dimension ranging from 5 nm to 200 nm.

15. The method of any one of clauses 1 or 3 to 12, wherein the slurry comprises insoluble motifs having a dimension greater than 200 nm.

Examples

Solution preparation and synthesis

All reagents were purchased from Sigma Aldrich and used without further modification. Varying M^{3+}: NO_3^- molar ratios from 1:0.7-1.154 of $M(OH)_3$, $MO(OH)$, or M_2O_3 powder to nitric acid (or other acids) are mixed under external ambient pressure forming slurry mixtures that range from 1 mM to 1 M metal content consistent throughout the reaction. The slurry is magnetically stirred at 60 °C until clear, resulting in complete solution dissolution. No further modification to the solution is done for solution phase spectroscopic measurements. For solid-state measurements aliquots of the solution were deposited on glass slides and allowed to crystallize for solid-state characterizations via Raman spectroscopy and single x-ray crystallography.

Solid state and solution characterization

Prior to analysis, each sample was filtered into the cuvette with a 0.1 PTFE μm syringe filter to remove any particulate matter. The following dynamic light scattering (DLS) and phase analysis light scattering (PALS) measured using the Mobiuζ from Wyatt technologies. DLS was used to measure the hydrodynamic radius (R_h) of the alumina species in solution. The Dynamics software uses the Einstein-Stokes equation ($R_h = K_b T/6\pi\eta D_t$) where K_b = the Boltzmann constant, T = temperature in kelvin, η = viscosity, and D_t = translational diffusion coefficient to solve for the R_h value.

Raman spectra were collected using an Alpha 300S SNOM confocal Raman microscope in a 180° backscattering configuration. A continuous wave pump laser provided ~50 mW of power with an excitation wavelength of 532 nm. A 0.3 m spectrometer equipped with 600 grooves/mm grating was used to detect stokes Raman scattering and provided a resolution of 1 cm^{-1}. The spectra from each sample were averaged over 100 accumulations at 1 second exposure times. The 520.5 cm^{-1} peak of Si was used as an internal standard.

FIG. 2 is a structural representation of various aluminum materials that were converted to flat-Al_{13} clusters via acidification according to the methods disclosed herein.

FIGS. 3A and 3B are optical microscope images of Al_{13} (FIG. 3A) and Ga_{13} (FIG. 3B) single crystal produced from the acidification process disclosed herein.

FIGS. 4A and 4B show dynamic light scattering of Al_{13} (FIG. 4A) and Ga_{13} (FIG. 4B) in 0.1 M aqueous solutions.

FIGS. 5A and 5B are solid state Raman spectra of Al_{13} (FIG. 5A) and Ga_{13} (FIG. 5B). Both spectra are consistent with previous reports of both clusters.

FIG. 6 is a powder x-ray of Al_{13} experimental compared with literature references.

Synthesis of aluminum Al_{13} Keggin ion by controlled dissolution of $Al(OH)_3$ in an aqueous monoprotic acid

The aluminum Al_{13} Keggin cluster $[(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}]$ is widely used in applications such as water treatment and flocculation. The current synthetic procedure to produce the cluster is addition of an aqueous base, e.g. NaOH, KOH, NH_3, or $Ca(OH)_2$ to an aqueous solution of $Al(NO_3)_3$ or $AlCl_3$. By adding 0.54 parts of a monoprotic strong acid to 1 part $Al(OH)_3$ under mild heating conditions (60 – 90 °C), the Keggin ion forms in high yield. The product of this synthesis has been scaled to liter quantities at concentrations as high as 1 M with respect to Al. This approach yields a material free of alkali, alkaline-earth, and transition-metal ions, leading to a protonated version of the material for water remediation and flocculation. FIG. 7 shows the NMR spectrum of the material synthesized using the traditional NaOH titration of $Al(NO_3)_3$ compared to this claimed dissolution method. Clearly, the spectra from acid addition match the characteristic spectrum for the Na-Keggin $[(NaAl_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}]$.

Additional work shows that the Al_{13} Keggin cluster $[(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}]$ can be used as a precursor for solution processed amorphous thin-film dielectric materials. Initial data from an MIS test structure suggests an improved quality of film properties using alumina precursors with decreased counterion concentration after annealing at 350 °C (FIG. 8).

In view of the many possible embodiments to which the principles of the disclosed compositions and methods may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention.

What is claimed is:

1. A method comprising:

reacting an aluminum mineral polymorph or a gallium mineral polymorph with an acid at an aluminum metal to acid molar ratio or gallium metal to acid molar ratio sufficient to produce M_{13} nanoscale clusters, M nano-agglomerates, or a M_{13} slurry, wherein M is Al or Ga.

2. A method comprising:

mixing an aluminum mineral polymorph or a gallium mineral polymorph with an acid to produce a slurry; and

processing the slurry under conditions sufficient to produce an aqueous solution of $M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$ nanoscale clusters, wherein M is Al or Ga.

3. The method of claim 1, wherein the M_{13} nanoscale clusters, M nano-agglomerates, or M_{13} slurry comprises $[M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]_a[X]_{15a}$, wherein a is an integer of 1 to 4, $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$, wherein b is an integer of 1 to 4, or a mixture thereof, wherein M is Al or Ga and X is a counterion derived from the acid.

4. The method of claim 1, wherein a or b is 1, and X is NO_3, Cl, I, Br, F, ClO_4, TsO, or MnO_4.

5. The method of claim 1, wherein the M_{13} nanoscale clusters comprise $[M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]_a[X]_{15a}$.

6. The method of claim 1, wherein the M_{13} slurry comprises $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$.

7. The method of any one of claims 1 or 6, wherein the aluminum mineral polymorph is selected from corundum, gibbsite, boehmite, diaspore, bayerite, nordstrandite, or any combination or mixture thereof.

8. The method of any one of claims 1 or 6, wherein the gallium mineral polymorph is selected from $Ga(O)OH$, Ga_2O_3, $Ga(OH)_3$, or any combination or mixture thereof.

9. The method of any one of claims 1 to 8, wherein the acid is selected from nitric acid, sulfuric acid, selenic acid, a halide acid, a sulfonic acid, a carboxylic acid, or a mixture thereof.

10. The method of any of claims 1 to 8, wherein the acid is nitric acid.

11. The method of any one of claims 1 or 7 to 10, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:0.3 mol eq of metal to acid to 1:1.3 mol. eq. of metal to acid.

12. The method of claim 2, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is greater than 1:0.7 mol eq.

13. The method of claim 11, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:0.3 to 1:0.65 mol eq to produce the slurry.

14. The method of claim 13, wherein the slurry comprises $[M_{13}O_4(OH)_{24}(H_2O)_{12})]_b[X]_{7b}$.

15. The method of claim 11, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:0.7 to 1:1.0 mol eq to produce the nano-agglomerates.

16. The method of claim 11, wherein the aluminum metal to acid molar ratio or gallium metal to acid molar ratio is 1:1.15 to 1:1.3 mol eq to produce the nanoscale clusters.

17. The method of claim 16, wherein the M_{13} nanoscale clusters comprise $[M_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]_a[X]_{15a}$.

18. The method of any one of claims 1 to 17, wherein the method is controlled to avoid formation of $Al(NO_3)_3$ or $Ga(NO_3)_3$.

19. The method of any one of claims 1, 3, 4, 7-11 or 16-18, wherein the nanoscale clusters have a dimension ranging from 1 nm to 5 nm.

20. The method of any one of claims 1, 3, 7-11, 15 or 18, wherein the nano-agglomerates have a dimension ranging from 5 nm to 200 nm.

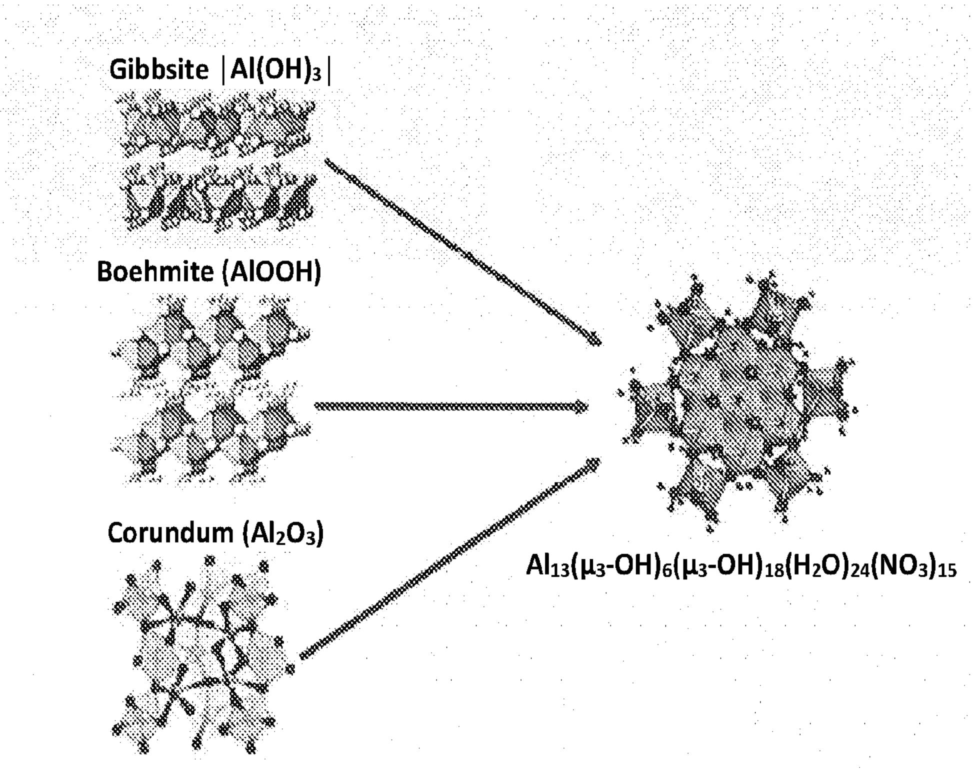
Gibbsite |$Al(OH)_3$|
Boehmite (AlOOH)
Corundum (Al_2O_3)
$Al_{13}(\mu_3\text{-}OH)_6(\mu_3\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}$

FIG. 1

$$13Al_2O_3\ (\text{Corundum}) + 26HNO_3 + 57H_2O \rightarrow 2[Al_{13}(OH)_{24}(H_2O)_{24}(NO_3)_{15}]$$

$$13Al(OH)_3\ (\text{Gibbsite}) + 15HNO_3 + 9H_2O \rightarrow Al_{13}(OH)_{24}(H_2O)_{24}(NO_3)_{15}$$

$$13Al(O)OH\ (\text{Boehmite}) + 15HNO_3 + 22H_2O \rightarrow Al_{13}(OH)_{24}(H_2O)_{24}(NO_3)_{15}$$

$$13Ga(O)OH + 15HNO_3 + 22H_2O \rightarrow Ga_{13}(OH)_{24}(H_2O)_{24}(NO_3)_{15}$$

$$13Ga_2O_3 + 26HNO_3 + 57H_2O \rightarrow 2[Ga_{13}(OH)_{24}(H_2O)_{24}(NO_3)_{15}]$$

$$13Ga(OH)_3\ (\text{söhngeite}) + 15HNO_3 + 9H_2O \rightarrow Ga_{13}(OH)_{24}(H_2O)_{24}(NO_3)_{15}$$

FIG. 2

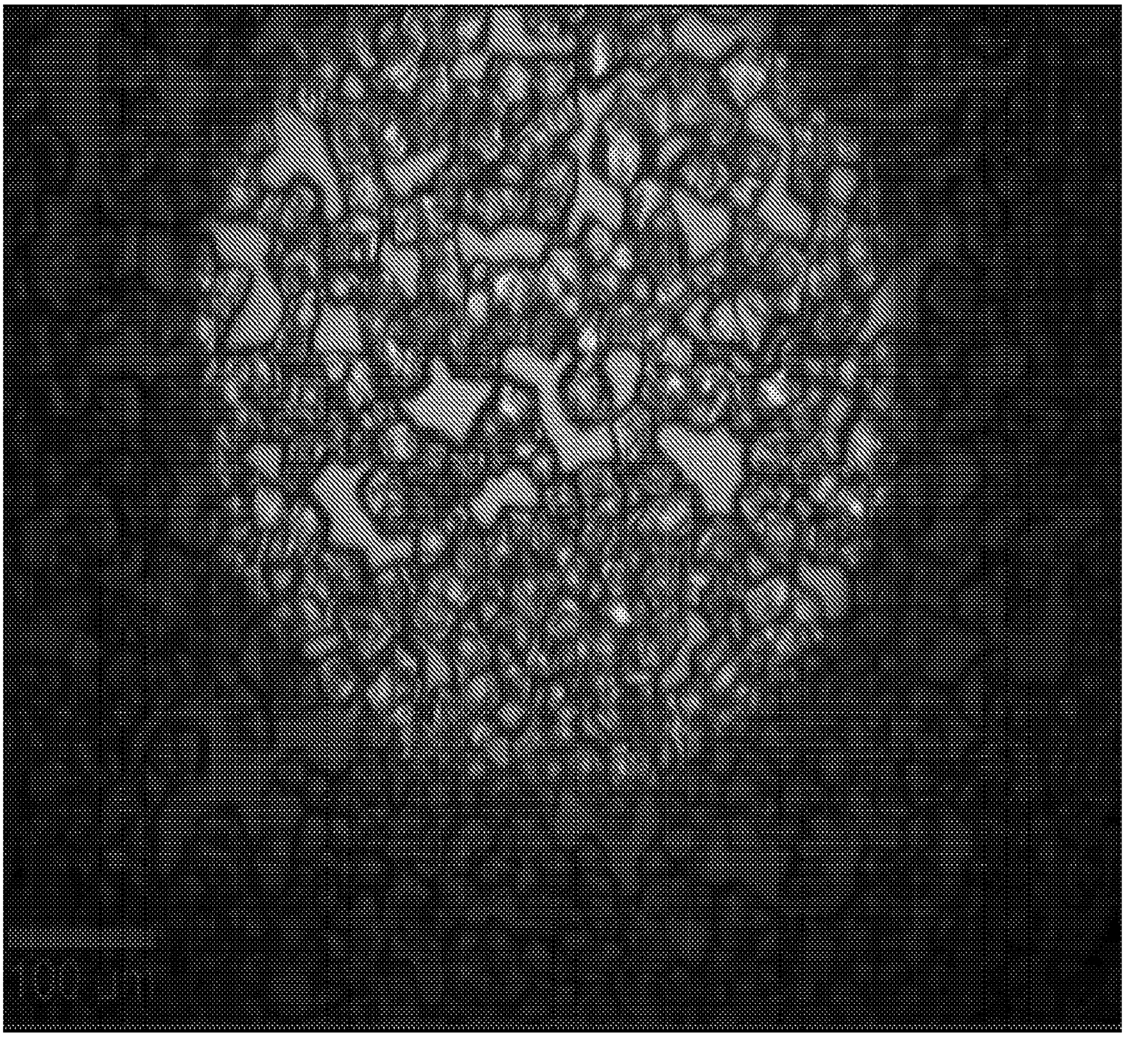

FIG. 3A

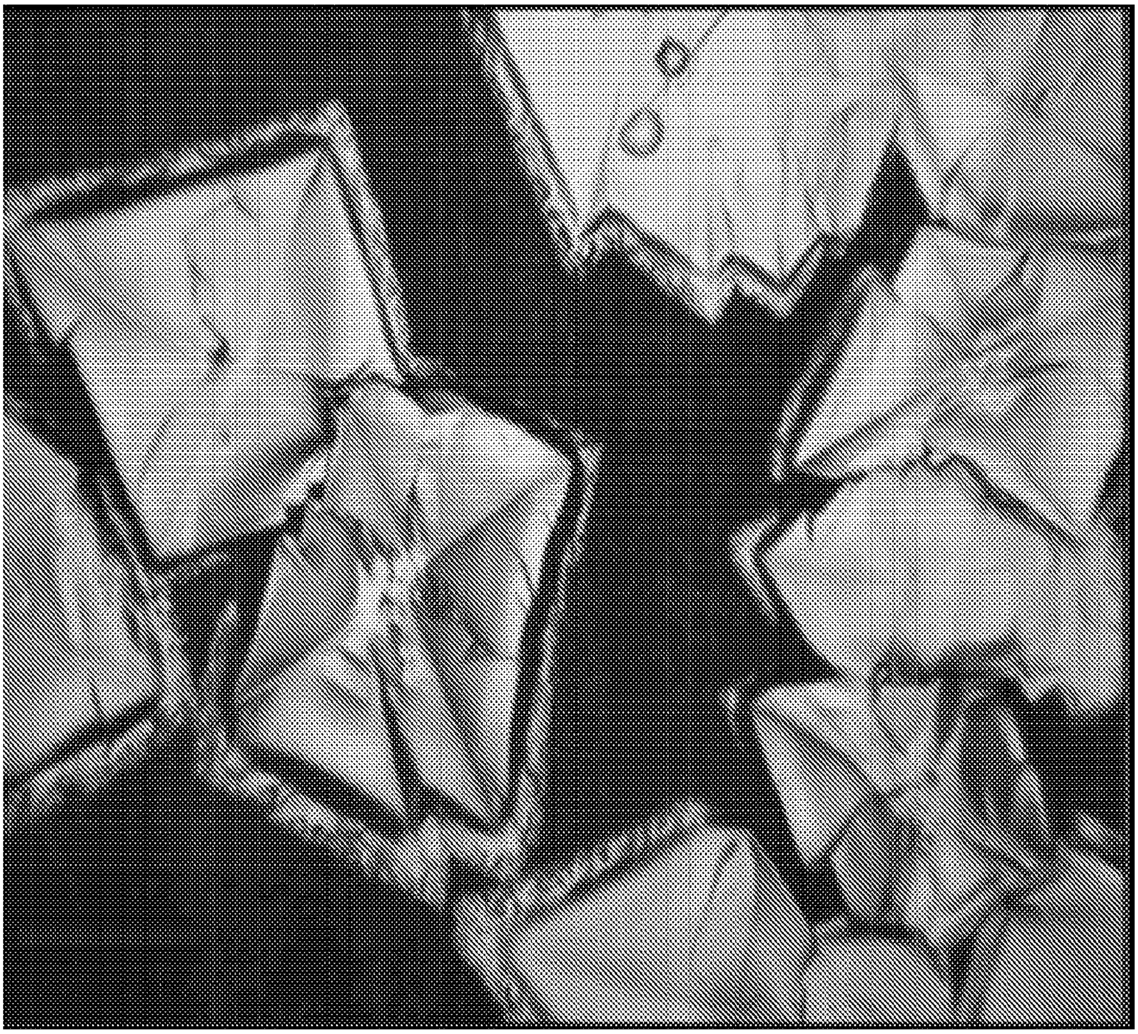

FIG. 3B

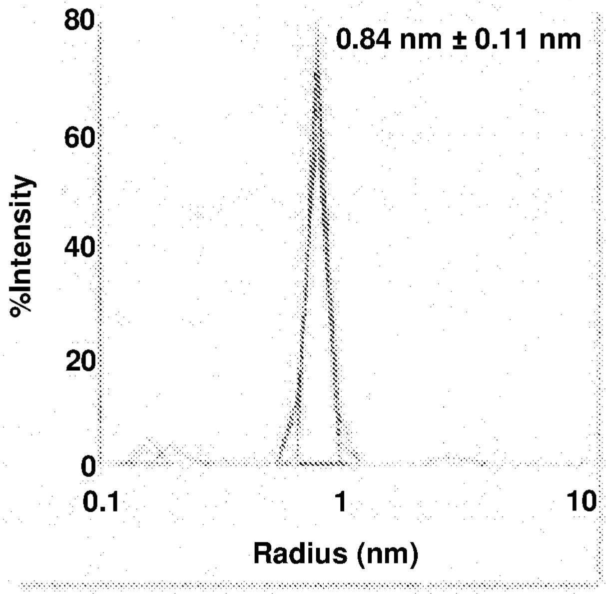
0.84 nm ± 0.11 nm
%Intensity
80
60
40
20
0
0.1
1
10
Radius (nm)

FIG. 4A

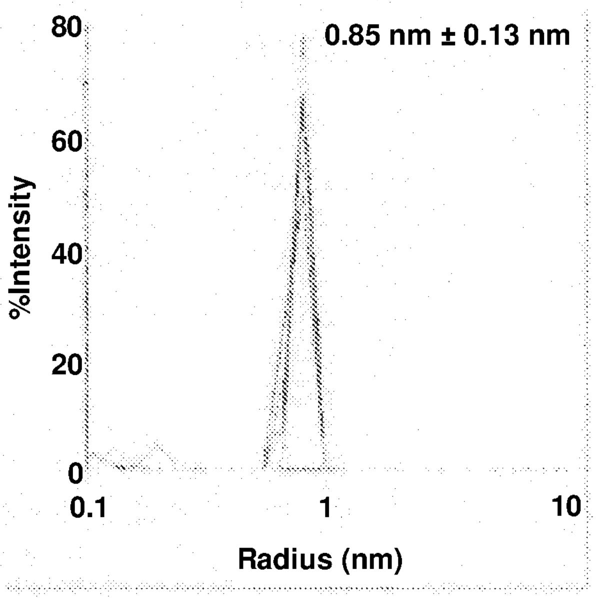
0.85 nm ± 0.13 nm
%Intensity
80
60
40
20
0
0.1
1
10
Radius (nm)

FIG. 4B

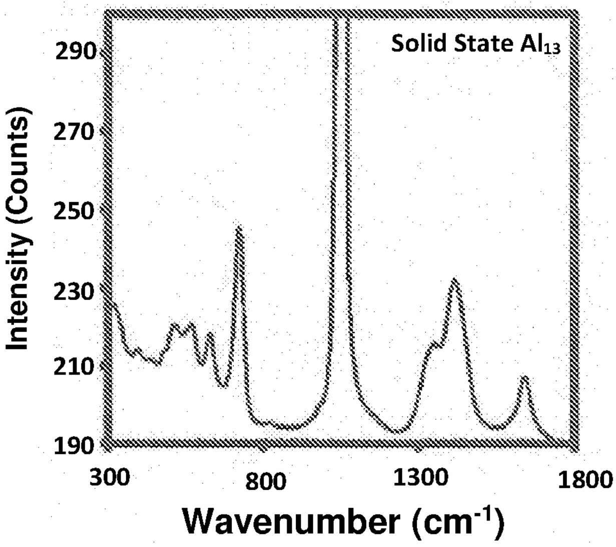
Solid State Al_{13}
Intensity (Counts)
290
270
250
230
210
190
300
800
1300
1800
Wavenumber (cm^{-1})

FIG. 5A

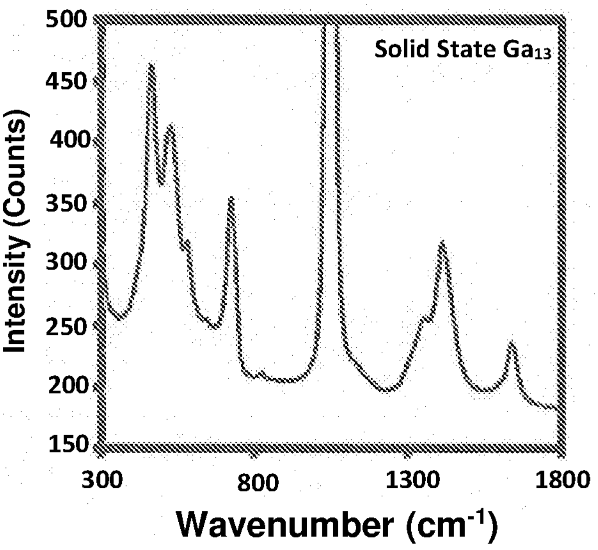
Solid State Ga_{13}
Intensity (Counts)
500
450
400
350
300
250
200
150
300
800
1300
1800
Wavenumber (cm^{-1})

FIG. 5B

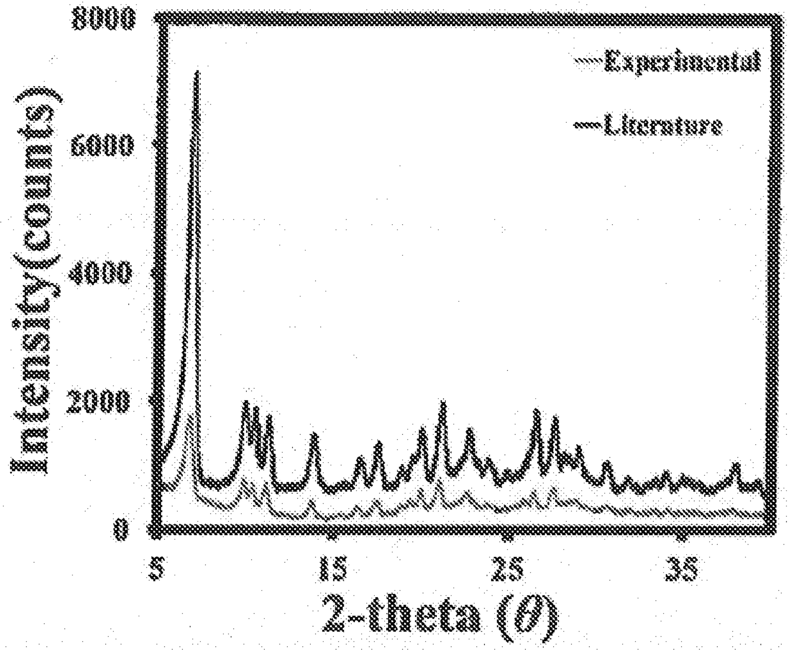
8000
6000
4000
2000
0
5
15
25
35
Intensity(counts)
2-theta (θ)
Experimental
Literature

FIG. 6

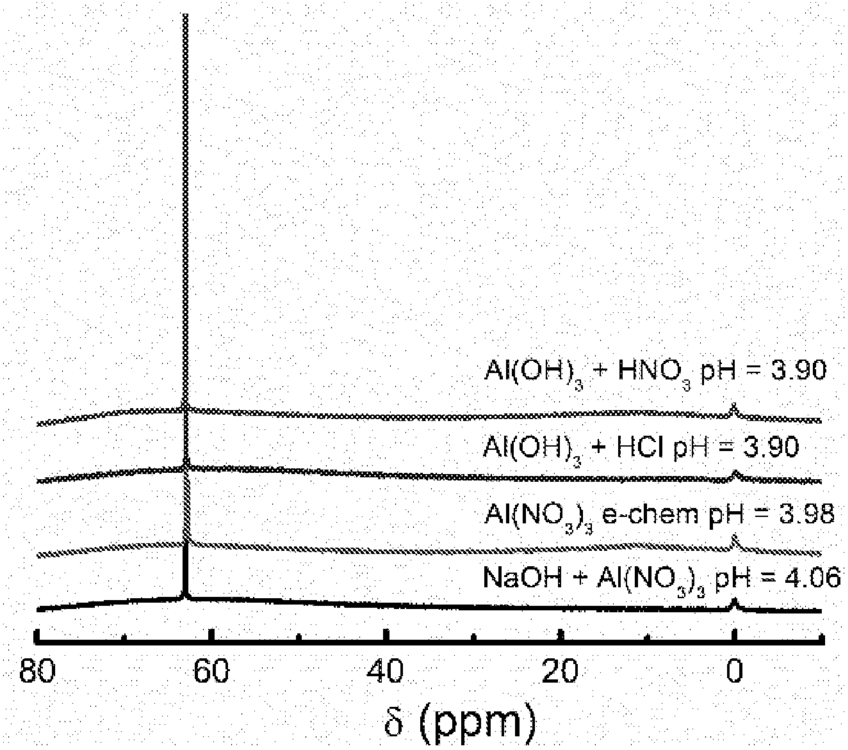
Al(OH)$_3$ + HNO$_3$ pH = 3.90
Al(OH)$_3$ + HCl pH = 3.90
Al(NO$_3$)$_3$ e-chem pH = 3.98
NaOH + Al(NO$_3$)$_3$ pH = 4.06
80
60
40
20
0
δ (ppm)

FIG. 7

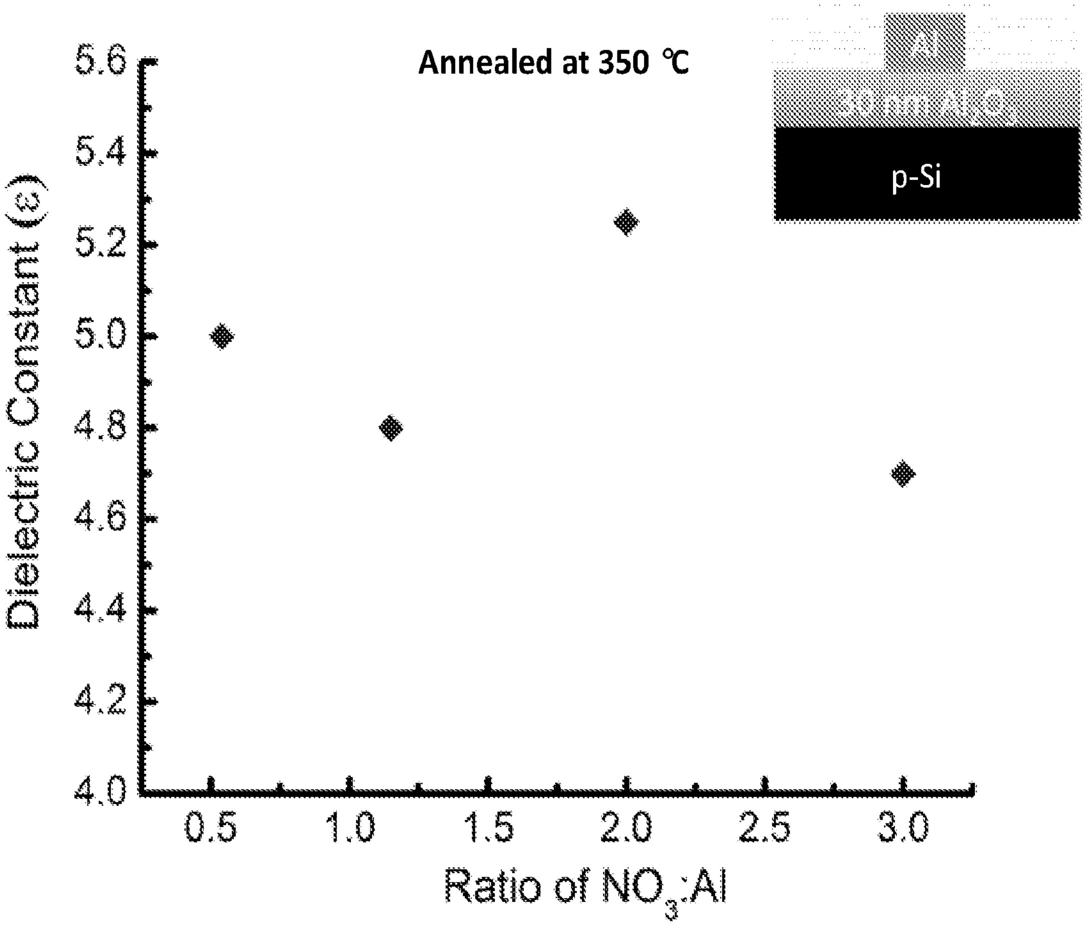
Annealed at 350 ℃
Al
30 nm Al_2O_3
p-Si
Dielectric Constant (ε)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
0.5
1.0
1.5
2.0
2.5
3.0
Ratio of NO_3:Al

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/041622

A. CLASSIFICATION OF SUBJECT MATTER

IPC (2016.01) C01F 7/02, C01F 7/20, C01F 7/24, C01G 15/00, B01J 13/00, B82Y 30/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2016.01) C01F, C01G, B01J, B82Y

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)
Databases consulted: THOMSON INNOVATION, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DROUIN J.M. et al. Rheology and structure of peptized boehmite pastes. Journal of Colloid and Interface Science, Volume 125, Issue 1, 1988, Pages 314-326, ISSN 0021-9797, http://dx.doi.org/10.1016/0021-9797(88)90080-X. 21 Jul 2004 (2004/07/21)	1-20
X	FRANCETIC V. et al. Peptization and Al-Keggin Species in Alumina Sol. Acta Chimica Slovenica, Volume 55, Issue 4, 2008, Pages 904-908, ISSN: 1318-0207. 31 Dec 2008 (2008/12/31)	1-20
X	OLIVERI A. Solution Characterization of Inorganic Nanoscale Cluster Species via 1H-NMR and DOSY. A dissertation presented to the Department of Chemistry and Biochemistry and the Graduate School of the University of Oregon in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December 2014, https://scholarsbank.uoregon.edu/xmlui/bitstream/handle/1794/18708/Oliveri_oregon_0171A_11146.pdf?sequence=1. 14 Jan 2015 (2015/01/14) Page 92, last paragraph – page 93, first paragraph.	1-20

☒ 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
"&" document member of the same patent family

Date of the actual completion of the international search 06 Nov 2016	Date of mailing of the international search report 06 Nov 2016
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616	Authorized officer ZAKHARIA Imad Telephone No. 972-2-5651686

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/041622

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
L	Google Scholar citation bibliographic details establishing the publication date of the document: [OLIVERI A. Solution Characterization of Inorganic Nanoscale Cluster Species via 1H-NMR and DOSY. A dissertation presented to the Department of Chemistry and Biochemistry and the Graduate School of the University of Oregon in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December 2014, https://scholarsbank.uoregon.edu/xmlui/bitstream/handle/1794/18708/Oliveri_oregon_0171A_11146.pdf?sequence=1], retrieved on 26 October 2016 (https://scholar.google.com/citations?view_op=view_citation&hl=en&user=m2V43sUAAAAJ&citation_for_view=m2V43sUAAAAJ:qjMakFHDy7sC). 26 Oct 2016 (2016/10/26)	1-20