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Hard coatings from metal boride nanocrystals ink

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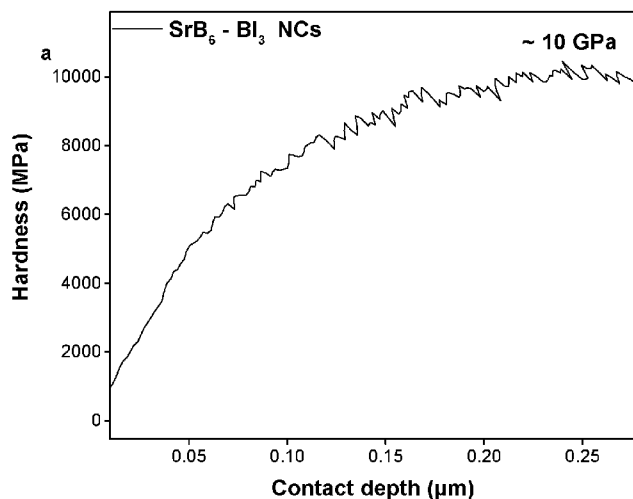
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Figures 7 A



(57) Abstract: The invention relates to an ink composition for depositing a coating on a substrate, comprising a colloidal dispersion of metal boride nanocrystals (NCs) in a liquid medium, wherein said metal boride NCs are selected from metal hexaborides (MB_6) and metal diborides (MB_2), and wherein said metal boride NCs are at least partly coated with a dispersing aid, wherein said dispersing aid is a ligand comprising a boron-binding moiety and wherein said metal boride NCs are present in said ink composition in a concentration of at least 10 mg/mL.



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Title: Hard coatings from metal boride nanocrystals ink

The invention relates to an ink composition, a solid composition suitable for
5 preparing such ink composition, a coating of a dried ink composition, methods of
producing such ink compositions, methods of coating an object with such ink
compositions and objects comprising a coating.

Metal borides constitute a class of compounds composed of a metal ion and a
boron network. Metal hexaborides (MB_6) and metal diborides (MB_2) form subclasses
10 of metal borides. The metal ion in MB_6 can be an alkali, transition, rare earth, or
actinide metal, which leads to a wide range of bulk physical properties. MB_6
compounds exhibit a simple cubic symmetry (Pm-3m) with the metal ion in 24-fold
coordination with a framework of boron octahedra (Figure 1a-b).

Diborides (MB_2) crystallize in the layered AlB_2 structure with a P6/mmm
15 hexagonal space group, where the metal atoms and boron atoms occupy with 1a (0,
0, 0) and 2d ($1/3, 2/3, 1/2$) positions respectively. The boron atoms form a honeycomb 2D
graphite – like sheets of boron atoms (borophene) alternating with hexagonal close
packed metal layers. Each metal is surrounded by six equivalent Metal neighbors in
metal planes and by 12 equidistant B neighbors, six above and six below. Each B has
20 the three B neighbors in the basal plane and metal atoms out of plane, three above
and three below.

MB_6 and MB_2 materials have a wide range of potential applications, including
thin and hard corrosion-resistant coatings. However, up to now, high-temperature
methods, such as chemical vapor deposition and the like, are required to prepare
25 such thin and hard coatings. Using high temperature methods is disadvantageous,
among others due to the high energy demand, requirement of special equipment, and
incompatibility with a wide range of substrates.

Processing such metal hexaborides and metal diborides as nanosized materials
in inks would solve one or more of the above-mentioned problems.

30 The inventors surprisingly realized that ink compositions comprising a
colloidal dispersion of MB_6 or MB_2 NCs may be prepared that are suitable for
preparing thin and hard coatings.

In particular, the inventors realized that it is required to obtain a relatively high
concentration of said metal boride NCs in said ink composition, to provide the desired

properties to a coating prepared from said ink composition. The inventors further found that such relatively high concentrations may be surprisingly obtained by at least partly coating the MB_6 and MB_2 NCs with specific dispersing aids.

Accordingly, the invention relates to an ink composition for depositing a coating on a substrate, comprising a colloidal dispersion of metal boride NCs in a liquid medium, wherein said metal boride NCs are selected from MB_6 and MB_2 , and wherein said metal boride NCs are at least partly coated with a dispersing aid, wherein said dispersing aid is a ligand comprising a boron-binding moiety and wherein said metal boride NCs are present in said ink composition in a concentration of at least 10 mg/mL.

Figures

Figure 1: (a) Divalent and trivalent metal cations which forms metal MB_6 ; (b) Crystal structure of MB_6 with boron forming octahedra (B_6) and metal cations occupying the center of the cubic cage of B_6 ; (c) XRD patterns for MB_6 NCs; (d) Raman spectra for MB_6 NCs; (e) Transmission electron microscopy (TEM) image of cubic shaped SrB_6 NCs; (f) Low magnification iDPC image of SrB_6 NCs, (inset) SrB_6 FFT (fast Fourier transform) and superimposed with cubic SrB_6 crystal structure overlapping metal and boron atoms; (g) Simulated iDPC STEM image of SrB_6 ; (h) Measured iDPC image of SrB_6 NC.

Figure 2: ^{11}B MQMAS spectra ss-NMR spectra of: (a) commercial B_2O_3 ; (b) commercial bulk LaB_6 ; (c) LaB_6 NCs; (d) LaB_6 TFSI; (e) LaB_6 OLA; (f) bulk SrB_6 ; (g) SrB_6 BI_3 ; (h) SrB_6 OLA; (i) HAADF – STEM image of SrB_6 /OLA NCs.

Figure 3: FT-IR of solid-state synthesized MB_6 NCs at 440 °C.

Figure 4: Photographs showing metal hexaborides before and after contacting with a solution of a dispersing aid. LaB_6 NCs in DMSO before (A) and after (B) contacting with TFSI solution. SrB_6 NCs in MFA before (C) and after (D) contacting with BI_3 solution. SrB_6 NCs in MFA before (E) and after (F) contacting with BTBA solution.

Figure 5: (a) XRD data of SrB_6 NCs (without any surface modification) and surface modified with BI_3 , OLA and standard bulk reference; (b) XRD of LaB_6 without modification, after modification with TFSI and OLA; (c) SrB_6 NCs pristine before surface modifications; (d) SEM image of OLA stabilized SrB_6 NCs (inset right: High

resolution HAADF TEM image of SrB₆ OLA NCs); (e) particle size histogram based on SEM image estimated using ImageJ software.

Figure 6: Photographs showing nickel borides before and after contacting with a solution of a dispersing aid. NiB₃ NCs in DMSO before (left hand panel of A) and after (right-hand panel of A) contacting with BTBA solution. NiB₃ NCs in MFA before (B) and after (C) contacting with TFSI solution. NiB₃ NCs in MFA before (D) and after (E) contacting with BI₃ solution.

Figure 7: Hardness (Figure 7A, C, E, G) and reduced modulus (Figure 7B, D, F, H) measurements of SrB₆ BI₃ and SrB₆ BF₄ thin films.

Figure 8: (a) X-ray diffraction patterns of HfB₂ NCs, performed with different molar ratio of Hf: B; (b) Stable HfB₂ NCs surface modified with BI₃ (0.024 mmol) in DMF after 48 hrs (right vials). A brown/orange colored solution was obtained after filtering the NCs using a 0.2 μm filter (left vials).

15 Detailed description

The term “or” as used herein means “and/or” unless specified otherwise.

The term “a” or “an” as used herein means “at least one” unless specified otherwise.

The term “essential(ly)” is generally used herein to indicate that it has the general character or function of that which is specified. When referring to a quantifiable feature, this term is in particular used to indicate that it is more than 90 %, more in particular more than 95 %, even more in particular more than 98 % of the maximum that feature. The term ‘essentially free’ is generally used herein to indicate that a substance is not present (below the detection limit achievable with analytical technology as available on the effective filing date) or present in such a low amount that it does not significantly affect the property of the product that is essentially free of said substance or that it is present in such a low amount (trace) that it does not need to be labelled on the packaged product that is essentially free of the substance. In practice, in quantitative terms, a product is usually considered essentially free of a substance, if the content of the substance is 0 - 0.1 wt.%, in particular 0 - 0.01 wt.%, more in particular 0 - 0.005 wt.%, based on total weight of the product in which it is present.

The term “about” in relation to a value generally includes a range around that value as will be understood by the skilled person. In particular, the range is from at least 10 % below to at least 10 % above the value, more specifically from 5 % below to 5 % above the value.

5 When referring to a “noun” (*e.g.* a compound, an additive *etc.*) in singular, the plural is meant to be included, unless specified otherwise.

 With the term “metal boride nanocrystals” as used herein is meant a crystalline form of metal borides, wherein at least one dimension is smaller than 100 nm, *e.g.* in a range between about one, preferably about ten angstrom and
10 about 100 nm, more preferably in a range between about one nanometer and about fifty nanometer, *e.g.* about five to forty nanometer.

 With the term “surface activation” as used herein is meant treatment, typically a chemical treatment, of a surface of a solid, *e.g.* a nanocrystal, to allow a reaction of one or more functional groups present on the surface with a reactant to
15 functionalize the surface. Typically, surface activation encompasses a step of at least partly removing a material which at least partly covers or shields one or more functional groups present on the surface, or conversion of unreactive groups present on the surface to reactive groups present on the surface, for example by means of oxidation, reduction or the like.

20 As used herein the term “surface functionalization” refers to a step of forming a bond between one or more functional groups present on the surface of a molecule, such as a nanocrystal, and a reactant, such as a dispersing aid, to form a molecule bound to said reactant. Said bond may refer to the formation of a covalent bond, which may be either reversible or irreversible, or the formation of a noncovalent
25 bond, such as stable hydrogen-bonding interaction or ionic bond.

 “Phase purity” is defined herein as NCs, wherein the inorganic core contains a single MB₆ or MB₂ phase. Phase-pure NCs may thus optionally contain an amorphous layer of a material other than the MB₆ or MB₂ NCs, for example a boron oxide layer (B₂O₃). However, phase-pure NCs do not contain NCs wherein
30 the inorganic core contains MB₆ or MB₂ in different space groups, nor in amorphous form.

 The term “polar” as used herein refers to a solvent that has a polarity index of 4 or more, as determinable by the method described in Snyder *et al.* (Snyder, 1974).

J. Chrom. A 92:223-230). Examples of polar solvents include methanol (polarity index of 5.1), ethanol (polarity index 4.3) and water (polarity index 10.2). The term “non-polar” as used herein refers to a solvent that has a polarity index of less than 4 (Snyder, 1974. J. Chrom. A 92:223-230). Examples of non-polar solvents include
5 heptane (polarity index of 0.1), hexane (polarity index of 0.1) and toluene (polarity index of 2.4).

With the term “protic solvent” as used herein is meant a solvent that is capable of donating a hydrogen atom to a suitable hydrogen acceptor. Typically a protic solvent comprises a hydroxyl group, carboxylic acid or amine group.
10 Examples of protic solvents include water and alcohols, such as methanol.

With the term “dispersion” as used herein is meant a mixture of a liquid medium and solid particles, wherein said solid particles are at least substantially homogeneously distributed throughout the liquid medium. A dispersion is at least substantially stable, meaning the solid particles do not settle in a defined amount
15 of time. Typically, a dispersion according to the invention is stable for 12 hours or more, in particular 24 hours or more. Said colloidal dispersion is typically considered essentially stable if the concentration of said metal boride NCs dispersed in said liquid medium deviates 10% or less from the initial concentration of said metal boride NCs in said liquid medium, preferably wherein the
20 concentration deviates 9% or less, more preferably 8% or less, even more preferably 7% or less, even more preferably 6% or less, even more preferably 5% or less, even more preferably 4% or less, even more preferably 3% or less, even more preferably 2% or less, even more preferably 1% or less, most preferably is essentially the same as the initial concentration. Stability of a dispersion is determinable by monitoring
25 the dispersion by eye, wherein settling of particles in a lower part of the dispersion typically indicates the dispersion is no longer stable or quantitatively, by determining the concentration of a dispersion after a set amount of time, as described herein in more detail below.

The invention is based on the inventive insight that powders of MB₆ and MB₂
30 NCs may be colloiddally dispersible in both polar and nonpolar media in high concentration to obtain versatile ink compositions that are suitable for applying a thin and ultrahard coating on a wide range of substrates, including flexible, textural and low-melting point substrates.

Accordingly, the invention relates to an ink composition for depositing a coating on a substrate, comprising a colloidal dispersion of metal boride NCs in a liquid medium, wherein said metal boride NCs are selected from MB₆ and MB₂, and wherein said metal boride NCs are at least partly coated with a dispersing aid, wherein said dispersing aid is a ligand comprising a boron-binding moiety and wherein said metal boride NCs are present in said ink composition in a concentration of at least 10 mg/mL.

Ink composition

10 Metal borides constitute a class of compounds composed of a metal ion and a boron network. According to the invention, said metal boride NCs are selected from MB₆ and MB₂ NCs. Preferably, said metal boride NCs are MB₆ NCs.

MB₆ NCs exhibit a simple cubic symmetry (Pm-3m) with the metal ion in 24-fold coordination with a framework of boron octahedra (see e.g. Figure 1a-b).

15 Without wishing to be bound by any theory, it is believed that the octahedra of boron is typically a key contributor to the physical properties of hexaborides. The bond length difference and shear anisotropy in hexaborides is electronically controlled by the nature and strength of the two types of B – B chemical bonds. Therefore, the strongly correlated electron system of MB₆ structure leads to unique electronic properties. Furthermore, the high strength of the B-B chemical bonds is envisaged to provide the material with high hardness and high melting temperatures.

Moreover, MB₆ advantageously have high melting points, high chemical stability, low expansion coefficients, and are refractory non-oxide metal-like compounds. These properties make MB₆ advantageously suitable for application in cutting-edge technologies including energy harvesting, heat absorption, quantum optics, ultra-hard and ultra-thin protective coatings.

The metal ion of MB₆ NCs preferably comprise alkali, transition, rare earth, or actinide metal, which leads to a wide range of bulk physical properties. Preferably, said metal ion is selected from Barium (Ba), Cerium (Ce), Calcium (Ca), Strontium (Sr) and Lanthanum (La).

Accordingly, said metal boride NCs preferably are MB_6 NCs, more preferably selected from lanthanum hexaboride (LaB_6), strontium hexaboride (SrB_6), calcium hexaboride (CaB_6), cerium hexaboride (CeB_6) and barium hexaboride (BaB_6).

In another preferred embodiment said metal boride NCs are MB_2 NCs.

5 The metal ion of MB_2 NCs preferably comprises a transition metal, preferably selected from Titanium (Ti), Vanadium (V) and Zirconium (Zr), Hf (Hafnium) and Magnesium (Mg).

Accordingly, said metal boride NCs are preferably MB_2 NCs selected from hafnium diboride (HB_2), titanium diboride (TiB_2), vanadium diboride (VB_2) and
10 zirconium diboride (ZrB_2).

Dispersing aids

Said dispersing aid is a ligand comprising a boron-binding moiety. Said boron-binding moiety has an ability to bind to a boron atom present on the surface
15 of said metal boride NCs. Hence, in said ink composition according to the invention, said dispersing aid is a ligand comprising a boron-binding moiety bound to a boron atom present on the surface of said metal boride NCs. As the skilled person will appreciate, said boron atoms present on the surface of said metal boride NCs includes both boron atoms incorporated in the metal boride NCs, as well as, if
20 present, boron atoms present in an amorphous boron oxide layer at least partly coating said metal boride NCs. Preferably, however, said boron atoms present on the surface of said metal boride NCs - bound by said boron-binding moiety - are boron atoms incorporated in the metal boride NCs.

Said boron-binding moiety may in principle be any atom or group that is
25 capable of binding said boron atoms present on the surface of said metal boride NCs.

Preferably, said boron-binding moiety comprises a boron atom, a nitrogen atom, a phosphide (P^{3-}), a fluoride (F^-), a chloride (Cl^-), a sulfide (S^{2-}) or a carboxylate group, more preferably a boron atom or a nitrogen group.

30 Said dispersing aid – when bound to said metal boride NCs - enables said metal boride NCs to form colloidal dispersion in a liquid medium.

Said dispersing aid may optionally further comprise a functional group suitable for keeping said metal boride NCs at least substantially colloiddally

dispersed in said liquid medium, or said boron-binding moiety of said dispersing aid may allow formation of said colloidal dispersion in said liquid medium.

As the skilled person will appreciate, the chemical composition of said dispersing aid will depend on the physicochemical of said liquid medium.

5 Typically, in embodiments wherein said liquid medium is a polar liquid medium, suitable dispersing aids for obtaining a colloidal dispersion of metal boride NCs typically comprise an ionic charge, preferably a negative charge. Alternatively or additionally, said ligand is preferably an inorganic ligand, meaning said ligand comprises no hydrocarbon groups.

10 Accordingly, in an aspect, said dispersing aid is preferably a dispersing aid which is suitable for keeping the metal boride NCs colloidally dispersed in a polar medium.

Alternatively, in embodiments wherein said liquid medium is a nonpolar liquid medium, suitable dispersing aids for obtaining a colloidal dispersion of metal
15 boride NCs in said nonpolar liquid medium, typically comprise a hydrophobic moiety, preferably an alkyl or alkenyl moiety, more preferably an alkyl moiety comprising a C₆-C₂₁ carbon chain.

Some ligands for preparing colloidal suspensions comprising nickel boride (Ni_xB) NCs for further solution processing applications have been described by
20 Hong et al. Chem Mater. 2023, 35, 1710-1722.

The inventors however surprisingly realized that successful ligands for obtaining a colloidal dispersion of nickel borides NCs, such as borane *tert*-butylamine (BTBA), were not suitable to prepare an colloidal dispersion of metal hexaborides and metal diborides (see Examples 1.2 and 2 and corresponding
25 Figures 4 and 7).

The inventors found that dispersing aids comprising a borane, a boron halide (BX₃, wherein X is a halide) or a sulfonimide were surprisingly suitable to obtain an colloidal dispersion of MB₆ and MB₂ in a suitable liquid medium. This finding is surprising as these ligands were unsuitable for preparing a colloidal dispersion of
30 nickel borides in a liquid medium (see Figure 7).

Accordingly, in an ink composition according to the invention, said boron-binding moiety preferably comprises a boron atom, more preferably a borane, a borate or a boron halide, even more preferably a borane selected from dodecaborate

and *closo*-B₆H₆ or a boron halide selected from boron iodide and boron chloride or tetrafluoroborate.

In a particularly preferred embodiment, said boron-binding moiety comprises a borane, preferably selected from dodecaborate and *closo*-B₆H₆. Without wishing to
5 be bound by any theory, it is envisaged that with such a dispersed aid, coatings may be prepared with a relatively high elasticity compared to other metal boride coatings, whilst maintaining sufficient hardness. This may be in particular advantageous in applications wherein said coating layer is provided to a flexible or textural substrate, e.g. a substrate having a relatively high roughness.

10 In another particularly preferred embodiment, said boron binding moiety comprises a boron halide, preferably boron triiodide or boron trichloride. Without wishing to be bound by any theory, it is believed that such dispersing aids promote epitaxial growth, thereby promoting formation of a thin, dense, layer with excellent hardness.

15 Alternatively or additionally, said boron-binding moiety comprises a nitrogen atom, preferably a sulfonimide, more preferably bis(trifluoromethane)sulfonimide.

Such dispersing aids are particularly suitable for an ink composition comprising a colloidal dispersion of metal boride NCs in a polar liquid medium.

20 Alternatively or additionally, said boron-binding moiety comprises a fatty amine or a fatty acid.

Said fatty amine or said fatty acid is typically an medium chain (C₆-C₁₂) or a long chain (C₁₃-C₂₁) fatty acid or fatty amine. Typically, said fatty acid or fatty amine has a carbon chain of at least 6 carbon atoms, preferably at least 7, at least 8, at least 9, at least 10, at least 11, at least 12, at least 13, at least 14, at least 15,
25 at least 16, at least 17, at least 18 carbon atoms. Preferably, said fatty acid or fatty amine comprises a carbon chain of between about 6 and about 21 carbon atoms, more preferably between about 12 and about 20, in particular between about 16 and about 19 carbon atoms.

Said fatty acid or said fatty amine may be a saturated or unsaturated amine.
30 Preferably said fatty acid or fatty amine is an unsaturated fatty acid or unsaturated fatty amine. Said unsaturated fatty acid may be a mono unsaturated fatty acid or a polyunsaturated fatty acid. Further, said one or more unsaturated bonds may be in cis or trans orientation.

Said fatty acid or fatty amine may further be linear or branched, preferably linear.

Examples of suitable fatty acids include stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:3), palmitic acid (C16:1), palmitoleic acid (C16:1),
5 arachidic acid (C20:0), gondoic acid (C20:1) and erucic acid (C22:1).

Examples of suitable fatty amines include oleylamine, hexadecylamine and palmitylamine, preferably oleylamine.

Such dispersing aids are particularly suitable for an ink composition comprising a colloidal dispersion of metal boride NCs in a nonpolar liquid medium.

10 Without wishing to be bound by any theory, it is believed that said alkyl or alkenyl moiety engages in hydrophobic interactions with said nonpolar liquid medium, thereby – when bound to said metal boride NCs – providing sufficient solubility in said liquid polar medium to form a colloidal dispersion. Accordingly, the invention further preferably relates to an ink composition according to the
15 invention, wherein said ligand comprises an alkyl group or alkenyl moiety, more preferably an alkyl moiety comprising a C₆-C₂₁ carbon chain.

Said metal boride NCs are at least partly coated with said dispersing aids. As the skilled person will appreciate, with at least partly coated is meant that a sufficient number of dispersing aids is present on the surface of said metal boride
20 NCs to obtain a colloidal dispersion. However, as the skilled person will appreciate, to obtain a colloidal dispersion it is not necessarily required that said metal boride NCs are fully coated with a coating of dispersing aids.

The density of said dispersing aids required on said metal boride NCs required to obtain a colloidal dispersion may be determined experimentally, e.g. by
25 gradually increasing the concentration of said dispersing aids or a precursor thereof in a method of preparing an ink composition according to the invention as described herein below.

The density of said dispersing aids on the surface of said metal boride NCs is usually at least about 5% of the surface of said NCs, more preferably at least 10%,
30 at least 15 %, in particular at least 15 %. Usually, the density of said dispersing aids is between about 5% and about 50%, preferably between about 10% and about 40%, in particular between about 20% and about 30% of the surface of the NCs.

Said density may be determined using elemental analysis, liquid and solid state NMR, or a combination thereof.

Said ink composition comprises a colloidal dispersion of said metal boride NCs in a liquid medium. Typically, said ink composition has a stability of at least 12 hours, more preferably at least 24 hours, at least 36 hours, at least 48 hours, at least 60 hours, at least 72 hours, in particular at least 1 week, most preferably at least 2 weeks, even more preferably at least 16 days, at least 18 days, at least 20 days, at least 22 days, at least 24 days, at least 26 days, at least 28 days, at least 30 days, at least 2 months, at least 3 months, at least 4 months, at least 5 months, most preferably at least 6 months. Preferably, said ink composition is stored at a temperature of about 25 °C in a concentration of about 20 mg/L. Such stability increases the potential of the ink composition as it need not be used immediately after preparation.

Herein stability may be determined by monitoring settling of metal boride NCs by eye, wherein observation of settling is considered an indication of loss of stability of said at least substantially stable dispersion.

Preferably, said stability is determined quantitatively, e.g. by determining the concentration of a dispersion after a set amount of time, such as after 24 hours, and comparing the concentration to the initial concentration of the dispersion (at $t=0$).

The concentration of a dispersion comprising metal boride NCs is preferably determined using a method comprising the steps of:

- a) Contacting metal boride NCs with a suitable solvent to obtain a dispersion of metal boride NCs, preferably to obtain a dispersion of metal boride NCs at a concentration of about 20 mg/L;
- b) Allowing the dispersion to stand for a desired amount of time, such as 24 h or more at a temperature of about 25 °C; followed by
- c) Filtering the dispersion, preferably over a filter with a pore size of 0.22 μm or less, to obtain a filtered dispersion;
- d) Removing the solvent from the filtered dispersion to obtain a solid fraction comprising metal boride NCs;
- e) Optionally drying the solid fraction;
- f) Determining the weight of the solid fraction; and

g) Comparing the weight of the solid fraction to the weight of the metal boride NCs contacted with a suitable solvent in step a).

Herein, the dispersion comprising said metal boride NCs is considered essentially stable if the weight of the dry dispersion deviates less than 10% from the weight of the metal boride NC's contacted in step a). Preferably, said weight deviates less than 9%, less than 8%, less than 7%, less than 6%, less than 5%, less than 4%, less than 3%, less than 2%, less than 1%, is preferably essentially the same as the weight of said metal boride NCs in step a).

10 *Properties of the ink composition according to the invention*

The inventors realized that a relatively high concentration of metal boride NCs in the ink composition is required to prepare a thin and hard coating therefrom.

Accordingly, in an ink composition according to the invention, the concentration of metal boride NCs is at least 10 mg/mL, preferably at least 20 mg/mL, more preferably at least 30 mg/mL, even more preferably at least 40 mg/mL, most preferably at least 50 mg/mL.

As the skilled person will appreciate the upper limit of said concentration depends on the liquid medium said metal boride NCs are dispersed in and may be experimentally determined by adding said metal boride NCs to a liquid medium until settling of said metal boride NCs is observed by eye or quantitatively using a method for determining a concentration of a dispersion, as described herein above.

Typically, said concentration is at most 500 mg/mL, more preferably at most 450 mg/mL, even more preferably at most 400 mg/mL, even more preferably at most 350 mg/mL, in particular at most 300 mg/mL, even more in particular at most 250 mg/mL, even more in particular at most 200 mg/mL, even more in particular at most 150 mg/mL, most preferably at most 100 mg/mL.

Accordingly, said concentration of said metal boride NCs in said ink composition is usually in the range from about 10 mg/mL up to about 500 mg/ml. Preferably said concentration is in the range of about 15 mg/mL to about 400 mg/mL, such as from about 20 mg/mL to about 300 mg/mL, more preferably between about 30 and about 200 mg/mL, most preferably between about 40 mg/mL and about 100 mg/mL. As the skilled person will recognize, the concentration of

metal boride NCs refers to the weight of metal boride NCs (in mg) per volume of liquid medium (in mL).

The ink composition according to the invention advantageously has a relatively narrow size distribution. This is important for obtaining a good quality of the coating. As will be understood, the particle size depends on the type of metal
5 boride and type of ligand.

Usually, the particle size of the metal borides range from between about 2 to about 20 nm, preferably between about 4 and about 16 nm, in particular between about 8 and about 12 nm. The average particle size is preferably between about 8
10 and about 14 nm, more preferably between about 10 and about 12 nm.

The particle size is determinable by SEM or TEM images, using the software ImageJ.

Method of preparing an ink composition according to the invention

15 The invention further relates to a method for preparing an ink composition according to the invention comprising:

(i) providing metal boride NCs, wherein said metal boride is selected from MB₆ NCs and/or MB₂ NCs;

(ii) subjecting the metal boride NCs to surface activation to obtain surface-
20 activated metal boride NCs; and

(iii) contacting the surface-activated metal boride NCs with a solution of a dispersing aid or a precursor thereof, in a polar liquid medium, wherein said dispersing aid or precursor thereof is a ligand comprising a boron-binding moiety to obtain an ink composition comprising metal boride NC's at least substantially
25 colloiddally dispersed therein.

Preferably, said metal borides provided in step (i) are prepared using a method comprising the steps

(a) contacting a metal chloride with a borohydride under inert atmosphere at a temperature below 1000 °C to obtain a crude mixture comprising metal boride
30 NCs;

(b) contacting the crude mixture with a protic solvent;

(c) collecting said metal boride NCs from the protic solvent;

(d) optionally washing the metal boride NCs collected in step (c) with a polar solvent;

Said metal borides are preferably prepared by contacting a metal chloride with a borohydride under inert atmosphere at a temperature below 1000 °C to
5 obtain a crude mixture comprising metal boride NCs.

Optionally, prior to said contacting, said metal chloride and said borohydride may be subjected to a step of (ball) milling. Typically, said metal chloride and said borohydride are (ball) milled for between about 10 minutes and about 1 hour, such as for about 30 minutes.

10 Further, optionally prior to said contacting, said metal chloride and said borohydride may be subjected to reduced pressure at a temperature of at least 80 °C, preferably at least 100 °C, more preferably at least 120 °C, such as about 140 °C to remove moisture from said mixture of metal chloride and borohydride, if present.

15 Exemplary reaction equations for obtaining MB₆ NCs suitable for preparing an ink composition according to the invention are described below.



Herein, X is preferably an alkali metal, preferably an alkali metal selected
20 from lithium and sodium.

Without wishing to be bound by any theory, it is believed that said borohydride (XBH₄) decomposes at the reaction temperature to form elemental boron (B) *in situ*, which subsequently reacts with the metal chloride precursor to form metal boride NCs.

25 Said borohydride may in principle be any borohydride that is capable of decomposing to form elemental boron. Examples include sodium borohydride, lithium borohydride, sodium cyanoborohydride, sodium triacetoxyborohydride, sodium triethylborohydride and lithium tri-sec-borohydride (L-selectride).

As the skilled person will appreciate, the reaction equations as described
30 above may be modified depending on the type of ligands present on the boron. Accordingly, in broadest form said borohydride may be defined by molecular formula XBHY₃, wherein X is as defined above and Y may be any ligand suitable to

form a stable borohydride. Preferably herein, Y is selected from H, a linear or a branched alkane, or an alkoxy group, more preferably an ester group.

Preferably, said borohydride comprises a borohydride having the molecular formula XBH_4 . With such borohydrides hydrogen gas is released, which may be relatively easily removed from the reaction mixture. Preferably, said borohydride is selected from sodium borohydride and lithium borohydride, more preferably sodium borohydride.

Preferably, said contacting comprises solid-state mixing of said metal chloride and said borohydride. Accordingly, step (a) is preferably carried out in absence of a solvent.

Said metal chloride and said borohydride are usually contacted in a molar ratio wherein said borohydride is present in a molar excess relative to said metal chloride. As the skilled person will appreciate the molar ratio depends on the type of metal boride NC is to be prepared.

For the preparation of metal hexaborides, said metal chloride and said borohydride are preferably contacted in a molar ratio of at least 1:6. However, to improve yield it is preferred if said metal chloride and said borohydride are contacted in a molar ratio of at least 1:8, more preferably at least 1:10, at least 1:12, such as at least 1:15.

Good results have been obtained with a molar ratio of metal chloride to borohydride of between about 1:8 to about 1:15, preferably about 1:10.

For the preparation of metal diborides, said metal chloride and said borohydride are preferably contacted in a molar ratio of at least 1:2, preferably at least 1:2.5, more preferably at least 1:3. Typical molar ratio's between metal chlorides and borohydrides are between about 1:2 and about 1:5, preferably about 1:3.

Advantageously, said contacting may be achieved at relatively low temperature compared to high-temperature methods known in the art to synthesize bulk metal borides. Said contacting is typically achieved at a temperature below 1000 °C, preferably below 900 °C, below 800 °C, below 700 °C, below 600 °C, below 500 °C, more preferably below 490 °C, below 480 °C, below 470 °C, below 460 °C, in particular below 450 °C.

Preferably, said contacting is achieved at a temperature of at least 300 °C, more preferably at least 320 °C, at least 340 °C, at least 360 °C, in particular at least 370 °C.

Usually, said contacting is achieved at a temperature of between about 300 °C and about 900 °C, in particular between about 320 °C and about 800 °C, 5 between about 340 °C and about 700 °C, between about 350 °C and about 600 °C, between about 360 °C and about 500 °C, in particular between about 370 °C and about 450 °C.

Said metal chloride is contacted with said borohydride for a time sufficient to 10 essentially complete the reaction, i.e. until one of the precursors, typically said metal chloride, has been essentially fully converted in said metal diboride.

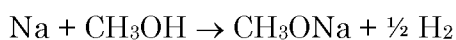
Typically said metal chloride is contacted with said borohydride for at least 10 minutes, preferably at least 30 minutes, more preferably at least 1 hour, even more preferably at least 2 hours, even more preferably at least 4 hours, even more 15 preferably at least 6 hours, even more preferably at least 12 hours, even more preferably at least 18 hours, in particular at least 23 hours. Such reaction times are typically sufficient to allow essentially all metal chloride to react with said borohydride.

Said metal chloride provides the metal ions present in the metal boride 20 nanocrystals. Accordingly, said metal chloride is preferably selected from cerium (III) chloride, barium(II) chloride, lanthanum (III) chloride, calcium (II) chloride, strontium (II) chloride, vanadium (III) chloride, titanium (IV) chloride and zirconium (IV) chloride, hafnium (IV) chloride and magnesium (II) chloride.

In step (a) a crude mixture comprising said metal borides is formed. Said 25 crude mixture may further comprise unreacted starting materials, in particular unreacted borohydride, byproducts and optionally side products. Examples of possible byproducts include alkali metals and alkali metal chloride salts, such as metallic sodium, sodium chloride, metallic lithium and lithium chloride.

In step (b) said byproducts are at least partly removed by contacting the 30 crude mixture with a protic solvent. This step usually involves deactivating (also referred to as 'quenching') of one or more of the byproducts, typically an alkali metal, by allowing it to react with said protic solvent thereby obtaining a solution

of said byproduct in said protic solvent. For example, if said byproducts at least comprise metallic sodium and sodium chloride, the reaction is as follows:



Preferably said protic solvent comprises a hydroxyl group, a carboxylic acid
5 group, and/or an ammonium group. Preferably, said protic solvent is an alcohol, water or an acid, in particular an alcohol, such as an alcohol selected from methanol, ethanol, propanol, isopropanol, butanol, *tert*-butanol and mixtures thereof, more preferably methanol.

Typically, said contacting of said crude mixture with said protic solvent is
10 achieved at a temperature of at most 30 °C, more preferably at most 25 °C, even more preferably at most 20 °C. Typically said contacting is performed at a temperature of between about 0 °C and about 25 °C, such as between about 5 °C and about 20 °C.

Preferably, said contacting of said crude mixture and said protic solvent is
15 achieved by slow addition of said protic solvent to said crude mixture.

Said crude mixture and said protic solvent are contacted for an amount of time sufficient to complete reaction of byproducts with said protic solvent. During the contacting, usually hydrogen gas is formed which is visualized as bubbles and may be used as indicator of completion of the reaction (e.g. the reaction may be
20 considered to have essentially completed when formation of bubbles has ceased).

Typically, said crude mixture and said protic solvent are contacted for at least 10 minutes, more preferably at least 30 minutes, such as at least 1 hour. Typically, said crude mixture and said protic solvent are contacted for between about 10
25 minutes and about 24 hours, preferably between about 30 minutes and about 16 hours, most preferably between about 1 hour and about 12 hours.

In step (c) said metal boride NCs are collected from said protic solvent. As substantiated herein, said protic solvent usually comprises one or more byproducts dissolved therein.

Said metal boride NCs may be collected from said protic solvent using any
30 suitable means in the art, for example by decanting or by centrifugation of the mixture followed by removing the liquid phase, e.g. by means of decanting or pipetting.

Optionally, said metal boride NCs may be dried to remove any residual protic solvent. Said metal boride NCs may be dried using any suitable means, such as in the oven or by using a heat gun. Optionally drying may be performed under reduced pressure to facilitate removal of residual protic solvent. As the skilled person will appreciate, the temperature required to dry said metal boride NCs depends on the boiling point of the protic solvent. Usually, said metal boride NCs are dried at a temperature of at least 50 °C, preferably at least 70 °C, such as between about 50 °C and about 150 °C, in particular between about 70 °C and about 120 °C.

10 Said metal boride NCs may optionally be subjected to one or more washing steps using a polar solvent, as defined in step (d). During said washing, typically one or more byproducts that were not removed in step (c) may be removed. For example, any species marked as XCl in the reaction equation above may be dissolved in said polar solvent and thereby separated from said metal boride NCs.

15 Said polar solvent may be any polar solvent suitable for at least substantially dissolving said XCl species. The skilled person may select a suitable polar solvent based on the reaction and the byproduct to be dissolved. Typically, said polar solvent is an aqueous solvent, an alcohol or a mixture thereof. Preferably said polar solvent is an aqueous solvent, preferably water.

20 Without wishing to be bound by any theory, it is believed that said one or more washing steps using a polar solvent may play a critical role and may decide the surface of the metal borides as defined herein. It is envisaged that during the washing process, the remaining boron precursors were oxidized to form an amorphous shell of boron oxide around the metal boride NCs, confirmed by solid-state NMR, electron microscopy, and FTIR (Figure 2).

25 Optionally, said metal boride NCs obtained in step (c) or (d) may be subjected to one or more drying steps to remove residual solvent, as described above.

Said metal boride NCs obtained after steps (a)-(c) and optionally (d) may be characterized using any suitable analytical methods known in the art, to determine their physical parameters, such as their purity or crystal structure. Suitable analytical methods include Raman spectroscopy, FT-IR spectroscopy, X-ray diffraction and transmission electron microscopy, for example using one or more of the methods described in Example 1.1.

Surface activation of metal boride nanocrystals

Said metal boride NCs are further subjected to a step of surface activation.

During the preparation of metal boride NCs, an amorphous boron oxide shell is usually formed, typically due to the presence of an excess of borohydride in step
5 a), which amorphous boron layer at least partly covers said metal boride NCs.

Without wishing to be bound by theory it is believed that the presence of said boron oxide shell on the outer surface of the metal boride NCs, strongly affects the functionalization of the surface by shielding surface boron atoms present in the metal boride NCs from undergoing a reaction with the ligands. This shielding effect
10 of the amorphous boron oxide coating was not envisaged, because the coating was also previously detected in other metal boride NCs, however not affecting the step of surface functionalization (see Figure 3h of Hong et al.).

Accordingly, the inventors found that it is required to subject said metal boride NC's to surface activation to obtain surface-activated metal boride NCs. As
15 the skilled person will appreciate, said metal boride NCs may be subjected to an intermediate step of surface activation, or said surface activation may be performed simultaneously with steps (i) or (iii), provided that surface activation is achieved prior to said contacting with a solution of a dispersing aid.

In principle said step of surface activation defined in step (ii) may be carried
20 out using any method known in the art suitable to at least partly remove said coating of boron oxide.

Preferably, said surface activation is achieved by contacting said metal boride NCs with an acid or a reducing agent.

Examples of suitable acids include hydrohalic acids, such as hydrochloric acid
25 and hydrobromic acid; sulfuric acid and nitric acid. Preferably, said acid is hydrochloric acid.

Said acid preferably has a pH of below 5, more preferably below 4, such as around 3. Preferably, said acid has a pH in the range of between about 0.5 and about 4, more preferably between about 2 to about 3.5.

30 Optionally, said surface-activated metal borides may be subjected to an aqueous washing step to remove residual acid and may optionally be subjected to a drying step. Said drying may be achieved at a temperature of at least 50 °C,

preferably at least 60 °C, in particular at least 70 °C, such as between 50 °C and 100 °C.

Alternatively or additionally, said surface activation may be achieved by contacting said metal boride NCs with a reducing agent. Examples of suitable
5 reducing agents include ammonia (NH₃), LiAlH₄, iodides (KI), hydrogen peroxide, hydrazine, citrates, SO₂ and SnCl₂, both SO₂ and SnCl₂ in the presence of HCl, NaBH₄, LiH, CaH₂, H₂ or CO gases.

Surface functionalization of metal boride nanocrystals

10 Said surface-activated metal boride NCs obtained in step (ii) are subsequently subjected to a step of surface functionalization as defined in step (iii). Because solubility of metal boride NCs in known solvents is limited, if not insoluble, surface functionalization with suitable dispersing aids is required to obtain a colloidal dispersion suitable for further solution-based processing methods.
15 During said surface functionalization, said boron-binding moiety of said dispersing aid forms a bond with boron atoms present on the surface of said metal boride NCs.

Accordingly, said surface activated metal boride NCs are subjected to a step of contacting the surface-activated metal boride NC's with a solution of a dispersing aid or a precursor thereof in a polar liquid medium, wherein said
20 dispersing aid or precursor thereof is a ligand comprising a boron-binding moiety, to obtain an ink composition comprising metal boride NC's at least substantially colloidally dispersed therein.

Without wishing to be bound by any theory, it is believed that by surface-functionalizing said (insoluble) metal boride NCs with a dispersing aid that is at
25 least substantially soluble in said polar solvent, said at least substantially soluble dispersing aid provide sufficient solubility to the functionalized metal boride NCs to obtain a colloidal dispersion in said polar solvent.

In step (iii), said dispersing aid or precursor thereof is a dispersing aid which is suitable for keeping the metal boride NCs at least substantially colloidally
30 dispersed in a polar medium, as defined herein above. Such a dispersing aid may also be referred to herein as "first dispersing aid", to distinguish from one or more further dispersing aids, even if no further dispersing aids are present.

As used herein, with the term “precursor thereof” is meant a molecule comprising said dispersing aid and optionally one or more functional groups. During said contacting as defined in step (iii), said dispersing aid is usually released and becomes bound to a boron atom present on the surface of said metal boride NCs to obtain a metal boride NC at least partly coated with said dispersing aid.

In principle any polar liquid medium or mixture of polar liquid media may be used, but preferably said polar solvent is an organic polar solvent or a mixture of two or more organic polar solvents. Examples include methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol, glycerol, 1,3-butanediol, ammonia, hydrazine, acetone, acetonitrile, benzonitrile, formamide, N-methylformamide (NMF), dimethylformamide, dimethylacetamide, dimethylsulfoxide (DMSO), hexamethylphosphoramide, propylene carbonate, N-methyl-2-pyrrolidone, nitromethane, methylamine, dimethylamine, ethylamine, propylamine, butylamine, triethylamine, trimethylamine, ethanolamine, methoxyethanol, ethylenediamine, dimethylethylenediamine, tetramethylethylenediamine, tetrakis(dimethylamino)ethylene, pyridine, 2,6-difluoropyridine, water and mixtures thereof.

Preferably, said polar liquid medium is selected from NMF, methylformamide, formamide and DMSO.

In step (iii) typically a weight to weight ratio of metal boride NCs to dispersing aid or precursor thereof of at least 1:1 is used. Preferably, a weight excess of said dispersing aid or precursor thereof is used. Preferably, said weight to weight ratio between said metal boride NCs and dispersing aid or precursor thereof is at least 1:1.1, more preferably at least 1:1.2, in particular 1:1.5, at least 1:2, such as at least 1:2.5.

Preferably, said concentration of dispersing aid or precursor thereof in said polar solvent is at least 0.001 M, more preferably at least 0.01 M, at least 0.05 M, at least 0.1 M, more preferably at least 0.2 M, in particular at least 0.25 M. Preferably, said concentration of dispersing aid or precursor thereof in said polar solvent is at most 0.5 M, more preferably at most 0.4 M, such as at most 0.3 M. Typical ranges of concentrations of inorganic ligand precursors in said polar

solvents are between about 0.001 M and about 0.5 M, preferably between about 0.01 M and about 0.4 M, between about 0.05 M and about 0.3 M.

Said contacting is typically achieved at a temperature below 200 °C, preferably below 180 °C, below 160 °C, below 140 °C, below 120 °C, more preferably
5 below 100 °C.

Preferably, said contacting is achieved at a temperature of at least 25 °C, more preferably at least 30 °C, at least 40 °C, at least 50 °C, at least 60 °C, at least 70 °C, at least 80 °C, in particular at least 90 °C.

Usually, said contacting is performed at a temperature of between about 30
10 °C and about 200 °C, preferably between about 50 °C and about 150 °C, in particular between about 70 °C and about 120 °C.

Said contacting is carried out for a time sufficient to obtain a dispersion of metal boride NCs in said polar solvent. Formation of said dispersion of metal boride NCs may be monitored by eye.

15 Typical reaction times for said contacting comprise at least 10 minutes, more preferably at least 30 minutes, more preferably at least 1 hour, even more preferably at least 2 hours, even more preferably at least 4 hours, even more preferably at least 6 hours, even more preferably at least 12 hours, in particular at least 16 hours. Usually, said contacting is performed for between about 10 minutes
20 and about 24 hours, preferably between about 1 hour and about 18 hours, more preferably between about 4 hour and about 16 hours.

Said dispersion of metal boride NCs in said polar liquid medium may be used directly in a method for coating an object, or may be subjected to one or more further steps such as one or more purification steps, a step of solvent exchange or a
25 step of contacting with a solution of a second dispersing aid or a precursor thereof, in a nonpolar liquid medium.

Optionally, said metal boride NCs may be precipitated from said polar liquid medium by addition of a nonpolar liquid medium. Said precipitated metal boride NCs may optionally be collected from said polar and nonpolar medium mixture to
30 obtain a solid composition comprising metal boride NCs at least partly coated with said dispersing aids. Said metal boride NCs may be optionally washed with a nonpolar liquid medium and optionally dried. Such a solid composition may be advantageously stored, transported or the like prior to redispersing said solid

composition in a polar liquid medium. Said polar solvent may be the same polar liquid medium as used in the method of preparing an ink composition according to the invention, or a different liquid medium.

Suitable nonpolar liquid media include hydrocarbons such as heptane,
5 hexane and pentane, and aromatic compounds such as toluene, benzene and xylene.

Accordingly, the invention further relates to a solid composition suitable for preparing an ink composition according to the invention, comprising metal boride NCs at least partly coated with a dispersing aid, wherein said metal boride NCs
10 are selected from MB₆ NCs and MB₂ NCs and wherein said dispersing aid is a ligand comprising a boron-binding moiety.

Said metal boride NCs and said dispersing aids are as defined herein elsewhere.

Said ink composition obtained in step (iii) may optionally subjected to one or
15 more further processing steps to form a metal boride NC at least partly coated with a second dispersing aid (also referred to in the art as “ligand exchange”). In such a method according to the invention, said ink composition obtained in step (iii) may be contacted with a solution of a second dispersing aid or a precursor thereof, in a nonpolar liquid medium.

Said second dispersing aid is distinguished from said first dispersing aid in
20 that the second dispersing aid, when bound to a boron atom of said metal boride NCs, allow said metal boride NCs to become at least substantially colloidally dispersible in a nonpolar liquid medium. This provides the ink compositions according to the invention with great flexibility, because it allows use of the
25 compositions in a wide range of liquid media and therefore enables their application for a wide range of purposes, such as the coating of a wide variety of substrates with various physicochemical properties.

Accordingly, the invention preferably relates to a method according to the invention, further comprising

30 (iv) contacting the ink composition obtained in step (iii) with a solution of a second dispersing aid or a precursor thereof, wherein said second dispersing aid or precursor thereof is a ligand comprising a boron-binding moiety in a nonpolar liquid medium to form a biphasic system; and

(v) allowing formation of metal borides NCs at least partly coated with said second ligands to obtain an ink composition comprising a colloidal dispersion of metal boride NCs at least partly coated with said second ligands in a nonpolar liquid medium.

5 In principle any nonpolar liquid medium or mixtures of nonpolar liquid media may be used in step (iv), including linear-, branched-, cyclic-, or halogenated alkanes, alkenes, and alkynes, as well as aromatic compounds. Nonpolar liquid media include but are not limited to pentanes, like n-pentane and 2,2,4-trimethylpentane, hexanes, like n-hexane, heptanes, octanes, nonane, decane ,
10 dodecane, hexadecane, 1-octadecene, petroleum ether, poly(α -olefin)s and oligo(α -olefin)s, squalane, cyclopentane, cyclohexane, benzene, toluene, ethylbenzene, xylenes, like p-xylene, trimethylbenzenes, cumene, chlorobenzene, dichlorobenzenes, 1,2,4-trichlorobenzene, fluorobenzene, difluorobenzenes, hexafluorobenzene, biphenyl, diphenyl oxide, cresols, terphenyls, mesitylene,
15 nitrobenzenen, tetralin, decalin, dichloromethane, trichloromethane, tetrachloromethane, carbon disulfide, trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, ethyl acetate, diisopropyl ether, diethyl ether and mixtures thereof.

Preferably said nonpolar liquid medium comprises an alkane, preferably
20 hexanes, heptanes or pentanes, or an aromatic solvent, preferably toluene, benzene or xylenes.

Said nonpolar liquid medium is essentially immiscible with said ink composition obtained in step (vi) to obtain a biphasic system. Said biphasic system, at least initially, comprises a first layer of a polar liquid medium comprising metal
25 boride at least partly coated with a (first) dispersing aid, and a second layer of a nonpolar liquid medium comprising said second dispersing aid or precursor thereof dissolved therein.

The nonpolar liquid medium is usually a poor solvent or poor dispersion medium for said first dispersing aid, including said metal boride NCs at least
30 partly coated with said first dispersing aid.

Preferably, the solubility of said first dispersing aid in the nonpolar liquid medium is below 0.1 mM. Preferably, the solubility of metal boride NCs

functionalized with said first dispersing aids in the nonpolar liquid medium is below 0.1 mg/L, or lower, e.g. below 0.01 mg/L, preferably essentially insoluble.

To improve said contacting of said ink composition obtained in step (iii) with said nonpolar liquid medium, the biphasic mixture is preferably (vigorously) stirred.

Said second dispersing aid or precursor thereof is a dispersing aid which is suitable for keeping the metal boride NCs at least substantially colloidally dispersed in a nonpolar liquid medium, as defined herein above. Preferably, said second dispersing aid comprises a fatty amine or a fatty acid, preferably oleylamine.

Preferably, the concentration of second dispersing aid in said nonpolar liquid medium is at least 0.001 M, more preferably at least 0.01 M, even more preferably at least 0.05 M, even more preferably at least 0.1 M, even more preferably at least 0.2 M, even more preferably at least 0.5 M, in particular at least 0.8 M. Preferably, said concentration of said second dispersing aid in said nonpolar liquid medium is at most 2 M, more preferably at most 1.8 M, such as at most 1.5 M. Typical ranges of concentration of second dispersing aids in said nonpolar liquid medium is between about 0.001 M and about 2 M, preferably between about 0.1 M and about 1.8 M, between about 0.5 M and about 1.5 M.

In step (iv) said contacting is typically achieved at a temperature below 200 °C, preferably below 180 °C, more preferably below 160 °C, even more preferably below 140 °C, even more preferably below 120 °C, even more preferably below 100 °C, most preferably below 50 °C.

Preferably, said contacting is achieved at a temperature of at least 0 °C, more preferably at least 5 °C, even more preferably at least 10 °C, even more preferably at least 15 °C, in particular at least 20 °C.

Usually, said contacting is performed at a temperature of between about 0 °C and about 50 °C, preferably between about 5 °C and about 40 °C, in particular between about 10 °C and about 30 °C, such as around 20 °C.

Said contacting is carried out for a time sufficient to obtain a dispersion of surface-functionalized metal boride NCs in said nonpolar liquid medium. Formation of said dispersion of surface-functionalized metal boride NCs may be monitored by eye, as described herein above.

Typical reaction times for said contacting comprise at least 10 minutes, more preferably at least 30 minutes, even more preferably at least 1 hour, even more preferably at least 2 hours. Typical reaction times include between about 10 minutes and about 12 hours, in particular between about 30 minutes and about 6
5 hours, such as between about 1 hour and about 4 hours.

Usually, upon completion of said contacting, said polar liquid medium may be removed from said non-polar solvent to obtain a colloidal dispersion of metal boride NCs in a nonpolar liquid medium. Any suitable method known in the art may be employed, such as pouring, decantation or pipetting. Advantageously this step
10 includes separation of said first dispersing aids or parts thereof from said metal boride NCs at least partly coated with said second dispersing aids in a nonpolar liquid medium.

Said colloidal dispersion of metal boride NCs in said nonpolar liquid medium may be used directly in a method for coating an object, or may be subjected to one
15 or more further steps such as one or more purification steps, or a step of solvent exchange.

Optionally, said metal boride NCs at least partly coated with said second dispersing aids in a nonpolar liquid medium may be precipitated from said nonpolar liquid medium by addition of a polar liquid medium. Said precipitated
20 metal boride NCs may optionally be collected from said polar and nonpolar liquid medium mixture to obtain a solid comprising metal boride NCs at least partly coated with said second dispersing aid. Said metal boride NCs may be optionally washed with a polar liquid medium and optionally dried.

Suitable polar liquid media for precipitation and washing include alcohols,
25 such as methanol and ethanol.

Said metal boride NCs may be redispersed in a nonpolar liquid medium, said polar liquid medium being the same as the polar liquid medium used in the reaction, or different.

30 *Methods for coating an object*

The invention further relates to a method for coating an object comprising, providing an object with a coating of an ink composition according the invention and allowing said coating to dry.

Said object may be coated using any suitable liquid-based coating method known in the art, such as drop casting, blade coating, spray coating, dip coating, doctor blading, spin coating, slot-die coating and bar coating. Preferably said object is coated using a drop casting, blade coating or spray coating method.

5 Said coating of ink composition may be allowed to dry using any suitable method known in the art. For example, said coating may be dried using elevated temperature. Advantageously, using a solution-based coating method, said coatings may be dried at a relatively low temperature.

10 Preferably, said coating is dried at a temperature of at most 200 °C, preferably at most 150 °C, more preferably at most 120 °C, even more preferably at most 100 °C, even more preferably at most 90 °C, even more preferably at most 50 °C, in particular at most 30 °C. Usual ranges are between about 15 °C and about 90 °C, in particular between about 20 °C and about 50 °C.

15 Alternatively or additionally, said coating may be dried by applying a flow to enhance vaporization of said solvent. For example, a flow of gas such as air or an inert gas may be used.

20 As will be understood the method of drying depends on the volatility of the liquid medium present in the ink composition. Typically, relatively high boiling liquid media such as DMF or DMSO are not easily evaporated, whereas relatively low boiling liquid media may be more readily evaporated using a flow of gas.

Optionally, said coatings may be subjected to a step of annealing the metal boride NCs together. Usually, annealing is achieved at a temperature of between about 50 °C and about 600 °C, preferably between about 100 °C and about 500 °C, more preferably between about 200 °C and about 400 °C.

25 Said annealing may be performed for an amount sufficient to prepare the coating. Typically between about 30 minutes and about 5 hours, such as between about 1 hour and about 4 hours. Without wishing to be bound by any theory, it is believed that annealing of the coating may lead to crystallization of the coating thereby removing any cracks which may be present in the coating, increase
30 toughness and increasing hardness of the coating.

Accordingly, the invention further relates to a coating of a dried ink composition according to the invention.

Advantageously, using relatively mild conditions to apply a coating to a substrate allows coating of a wide range of substrates. Said substrate may be selected from metallic substrates, glass, plastic, sapphire wafers, silicon wafers, quartz, ceramics, synthetic substrates, composites, textiles, paper and wood.

5 Preferably said substrate is a flexible and/or textured substrate. As used herein, a flexible substrate is meant to be understood as a substrate that can be bend without inducing cracking or creasing. Typically, a flexible substrate has a young modulus of at most 1 GPa, preferably at most 0.5 GPa, at most 0.1 GPa, at most 0.01 GPa, such as between about 0.001 GPa and about 0.1 GPa. With the
10 term textured substrate is meant a substrate that is characterized with a relatively high roughness. Roughness can be determined using any suitable method known in the art, such as for example using a profilometer or a laser scanner. Preferably, said material has a roughness value (Ra) of at most 10 μm , preferably at most 5 μm , more preferably at most 1 μm . Preferably, said material has a roughness
15 value of at least 0.1 nm, preferably at least 0.5 nm. Typically the roughness value of the material is in the range of between about 0.1 nm and about 10 μm , preferably between about 0.5 nm and about 5 μm .

Alternatively or additionally, said substrate is a substrate having a relatively low melting point, preferably a melting point of below 500 $^{\circ}\text{C}$, more preferably
20 below 400 $^{\circ}\text{C}$, even more preferably below 350 $^{\circ}\text{C}$, even more preferably below 300 $^{\circ}\text{C}$, even more preferably below 250 $^{\circ}\text{C}$, even more preferably below 200 $^{\circ}\text{C}$, even more preferably below 150 $^{\circ}\text{C}$, even more preferably below 100 $^{\circ}\text{C}$, even more preferably below 90 $^{\circ}\text{C}$, even more preferably below 80 $^{\circ}\text{C}$, even more preferably
25 below 70 $^{\circ}\text{C}$, even more preferably below 60 $^{\circ}\text{C}$, even more preferably below 50 $^{\circ}\text{C}$, even more preferably below 40 $^{\circ}\text{C}$, such as below 30 $^{\circ}\text{C}$. Preferably said melting point is at least 20 $^{\circ}\text{C}$, more preferably at least 30 $^{\circ}\text{C}$, even more preferably at least 40 $^{\circ}\text{C}$, even more preferably at least 50 $^{\circ}\text{C}$, even more preferably at least 60 $^{\circ}\text{C}$, even more preferably at least 70 $^{\circ}\text{C}$, even more preferably at least 80 $^{\circ}\text{C}$, even more preferably at least 90 $^{\circ}\text{C}$, even more preferably at least 100 $^{\circ}\text{C}$, even more
30 preferably at least 200 $^{\circ}\text{C}$, even more preferably at least 300 $^{\circ}\text{C}$. Preferably, said melting point is in the range of between about 20 $^{\circ}\text{C}$ and about 350 $^{\circ}\text{C}$, preferably between about 30 $^{\circ}\text{C}$ and about 200 $^{\circ}\text{C}$, more preferably between about 40 $^{\circ}\text{C}$ and about 100 $^{\circ}\text{C}$.

Such substrates can advantageously be coated using a method according to the invention, but coating thereof is not feasible using conventional high-temperature coating methods, due to melting of the substrate.

Said melting point is determinable using any suitable method known in the art. As used herein, the melting point refers to the temperature that the substrate starts to melt or deform, which melting or deformation typically effects the functionality of said substrate, for example when present in an object.

The invention further relates to an object comprising a coating according to the invention.

Said object preferably comprises a substrate coated with said coating, wherein said substrate is preferably a flexible and/or textured substrate and/or a substrate with a relatively low-melting point, as defined herein above.

Advantageously, coatings according to the invention, preferably having a hardness and Young's modulus as defined herein, have the potential to withstand high forces and incompressibility. Therefore, such coatings are suitable in a wide range of applications.

Accordingly, said object may be an vehicle or a part thereof, such as an aircraft or a part thereof, an electronic device, a medical device, a plasma display, a thermoelectric material, a solar panel or the like.

Said coating may vary in thickness depending on the application. Preferably, said coating has a thickness of at most 100 μm , more preferably at most 50 μm , even more preferably at most 10 μm , even more preferably at most 5 μm , even more preferably at most 3 μm . Usually, said coatings have a thickness in the range of between about 1 nm to about 100 μm , preferably between about 10 nm and about 50 μm , between about 100 nm and about 10 μm .

Said thickness is determinable by profilometry measurements, using Bruker Dektak XT profilometer, for example using the following method: The substrates coated with films were scratched using a sharp glass tip (very thin scratch) through the film until the surface of the substrate is visible. The scratched film substrate is placed in the sample holder, the XY station helps to move the sample with respect to the tip which maps the surface profile. The tip moves across the scratch on the film measuring the depth of the scratch, which is the actual thickness of the film.

Said coatings advantageously have relatively high hardness. Preferably, said coating has a hardness of at least 150 MPa, more preferably at least 200 MPa, even more preferably at least 500 MPa, even more preferably at least 1 GPa, even more preferably at least 3 GPa, most preferably at least 5 GPa. Usually, the hardness of
5 said coatings is between about 150 MPa and about 30 GPa, preferably between about 200 MPa and about 20 GPa, more preferably between about 250 MPa and about 15 GPa, such as between about 1 GPa and about 10 GPa.

Said coating advantageously has preferably a reduced modulus (Young's modulus) of at least 20 GPa, more preferably at least 50 GPa, even more preferably
10 at least 100 GPa, in particular at least 150 GPa. Preferably said coating has a reduced modulus in the range of between about 20 to about 300 GPa, preferably between about 50 GPa to about 250 GPa, in particular between about 100 and about 200 GPa.

The reduced modulus is defined by the formula $Z = E / (1 - \nu)$; where E is
15 elastic moduli or young's moduli which measures stiffness: ν is Poisson's ratio (lateral contraction of a materials when it is stretched in one direction).

Said hardness and said elastic modulus is determinable using a FT-I04 Femto-indenter manufactured by Femto tools consisting of high resolution bi-axial force sensor, for example as described in Example 4.

20 For the purpose of clarity and a concise description, features are described herein as part of the same or separate embodiments, however, it will be appreciated that the scope of the invention may include embodiments having combinations of all or some of the features described.

The invention is demonstrated by the following examples.
25

Examples

1.1 Materials

Lanthanum (III) chloride (LaCl_3 , anhydrous beads ≥ 99.99 % trace metal basis), Cerium (III) chloride (CeCl_3 , anhydrous beads ≥ 99.99 % trace metal basis), Barium (II) chloride, N-Methyl formamide, and formamide (99%), Chloroform (>99.8%), Poly(methyl methacrylate) (PMMA) ($M_w \sim 350,000$), Oleylamine (90%), Bis(trifluoromethane)sulfonimide (>95 %) were all purchased from Sigma Aldrich. Strontium (II) chloride (anhydrous 99.99 %) from Acros, Calcium (II) chloride (anhydrous, 96%), methanol (99.8%), dimethyl sulfoxide (DMSO, 99.9 %), toluene (99.85 %), and ethanol (99.5%), were purchased from Fischer scientific. Sodium borohydride (98 + %) powder manufactured by Acros organics was supplied by Fischer scientific.

1.2 Characterization Methods

1.2.1 Powder X-ray Diffraction Patterns (pXRD)

Bruker D8 Advance diffractometer equipped with theta–theta Bragg–Bretano geometry was used to record pXRD patterns and operated at 40 kV and 40 mA on a Cu X-ray tube. Rietveld refinement was performed. The Rietveld refinement was performed using Profex software: D8 Bruker configuration (RDMS-D8-15LynxEyeXE), Goniometer radius 350 mm, minimum angle 2° , maximum angle 150° , CU wavelength 1.5406 \AA , constant number of background coefficients 10, Xray tube ; target width 12.0 mm apparent height 0.0400 mm: divergence slit ; distance from sample 250 mm, irradiated length 15 mm: Soller slit opening angle 0.0218 radians: axial beam mask width 10.50 mm, distance from sample 300 mm: anti-scatter slit mode fixed, distance from sample 260 mm, slit opening 9 mm.

1.1.2 IR Spectroscopy

A Shimadzu IRSpirit Fourier transform infrared (FTIR) instrument in transmittance mode, apodization Happ-Genzel, 16 number of scans and resolution of 8 were used to measure the Spectra.

1.1.3. Scanning Transmission Electron Microscopy (STEM)

STEM with nanometer-resolution was operated using an FEI Helios G4 CX at 18 kV in transmission mode. With a monochromatic, probe and image corrected Thermo Fisher Scientific Themis Z S/TEM system operating at 300 kV an atomic resolution
5 STEM imaging was conducted. In the second case, two imaging modes were employed: high-angle annular dark-field (HAADF) and integrated differential phase contrast (iDPC) (108,135,136) using ~80% coverage of a 4-segmented DF detector. The measured beam convergence angle was ~24.0 mrad (point resolution 70 pm) where a probe current of 25 pA was used. Velox software was used for data
10 acquisition and analysis. Simulation was performed using Dr. Probe software. ¹ The STEM samples were prepared on support film, Carbon Type B, 400 mesh, Cu (Ted Pella, Inc. 01814-F) and dried overnight in the antechamber of the glovebox. The low magnification imaging was performed using FEI helios G4 CX operated at 18 kV in transmission mode, and JEOL 2010 high resolution electron microscope
15 with an accelerating voltage of 200 KV. The images were processed and analyzed using Gatan microscopy suit software and ImageJ.

1.1.4 Thermogravimetric Analysis (TGA)

TGA analysis was performed using PerkinElmer TGA 4000. The measurement was
20 done with temperature range of 35–900 °C and heating rate of 10 °C/min under nitrogen gas flow.

1.1.5 ICP-MS

ICP-MS measurements were carried out by using ICP-MS/MS iCAP TG Thermo
25 Scientific. All the samples were prepared through acid digestion. A small amount of the sample was weighed in a polypropylene cup, and 100 µL of 32.5% or 65% HNO₃ was added. Subsequently, 400 µL of water was added for sample dissolution.

1.1.6 Solid-state NMR

30 Solid-state ¹¹B NMR spectra were recorded on a 500 MHz Bruker spectrometer (11.7 T) equipped with an Avance Neo console and a 1.3 mm three-channel low temperature magic-angle spinning probe. The solid state parameters are shown in Table 1. Samples were packed into 1.3 mm zirconia rotors and spun up at 33.333 or

40 kHz spinning speed using dry nitrogen gas. Powdered NaBH₄ was used as secondary reference for chemical shifts (-42.06 ppm relative to BF₃·OEt₂) and as pulse calibration standard as its quadrupole interaction is assumed to be negligible.

2 Quantitative ¹¹B solid-state NMR spectra were recorded using a short, strong
5 radiofrequency pulse of 0.34 μs, which corresponds to a flip angle inferior to $\frac{90^\circ (NaBH_4)}{2(2I+1)} = 11.3^\circ$. Up to 256 transients were cumulated using relaxation delays of 5*T₁.

The spectra were fitted using the dmfit software (Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G.
10 Modelling one- and two-dimensional solid-state NMR spectra. *MAGN RESON CHEM* **2002**, *40* (1), 70-76.).

The ¹¹B 3QMAS NMR spectra were acquired at 33.333 kHz sample spinning frequency using the 3-pulse sequence with z-filter. The excitation, conversion, and detection pulses lasted 4.3, 1.1, and 5 μs, respectively. Up to 128 t₁ slices of 240 scans
15 were acquired with a t₁ increment of 30 μs and the spectra were processed using the topspin software (Amoureux, J.-P.; Fernandez, C.; Steuernagel, S. ZFiltering in MQMAS NMR. *J. Magn. Reson.* **1996**, *123* (1), 116-118. Massiot, D.; Touzo, B.; Trumeau, D.; Coutures, J. P.; Virlet, J.; Florian, P.; Grandinetti, P. J. Two-dimensional magic-angle spinning isotropic reconstruction sequences for
20 quadrupolar nuclei. *Solid State Nuclear Magnetic Resonance* **1996**, *6* (1), 73-83.).

Table 1: Solid state NMR parameters

Sample	Quanti @ 40 kHz	Selectif @ 40 kHz	Quanti @ 33 kHz	Selectif @ 33 kHz
B ₂ O ₃	101	102	105	106
Bulk LaB ₆	601	602	603	604
LaB ₆	201	202	203	204
SrB ₆	301	302	303	304
SrB ₆ BI ₃	401	402	403	404

1.1.7 Raman spectroscopy

25 A confocal Raman microscope (Renishaw, inVia Qontor) was used to measure the Raman spectra. Raman spectra were taken in reflection geometry using an objective with 50x magnification in the ambient atmosphere. A 532 nm continuous wave laser was used as an excitation source, and the spectra were collected using

the provided edge filters and an 1800 l/mm grating. (Power: 1%; Exposure time: 5 s; Accumulations: 20)

1.1.8 Absorption spectra

5 The absorption spectrum of the solution was acquired with a Shimadzu UV3600 spectrometer background corrected for the pure solvent from 200 nm to 200 nm, at medium scan speed, slit width of 8 nm, light source change wavelength at 310 nm; detector change wavelength at 870 nm and 1650 nm; grating change wavelength at 720 nm. The thin films on quartz films were measured with slit width of 32 nm in
10 an integrated sphere attachment. The baseline was performed on PMMA coated quartz films.

Example 1: Solid state Synthesis of MB₆ (M= Sr, La, Ce, Ca, Ba) NCs

The synthesis of MB₆ were carried out through solid state reaction using the method
15 as described by Hong et al. Chem mater. 2023, 35, 1710-1722 with modification as indicated below.

Metal chloride (MCl_x) and NaBH₄ solid precursors (molar ratio MCl_x to NaBH₄ 1:10) were ball-milled for 30 minutes in a sealed air-tight container with 20 zirconium
20 balls at 800 RPM before the reaction. All initial preparations were done inside a glove box and then transferred to an Argon flow Schlenk line. The reactants were taken in a 25mL round bottom flask connected to a water-cooled condenser. All steps in the reaction process were carried out under Argon atmosphere using the Schlenk line. The reaction mixture in the round bottom flask was first subjected to vacuum
25 then stirred using a glass stirrer at 140 °C for an hour to remove moisture from the starting materials. Subsequently, the reaction was further heated and allowed to proceed at 440 °C for 23 hours.

After the completion of the reaction, the reaction was brought to room temperature
30 and methanol was added to quench the sodium, which was formed as a by-product during the reaction. The product was stirred overnight in methanol, to completely quench the sodium. Methanol wash was performed once again and centrifuged at 11000 RPM for 5minutes. The solid precipitate obtained from the methanol wash

was quickly oven dried at 70 °C and washed with water (3x times). The washed precipitate was left in 0.5 M HCl (5 ml) at room temperature overnight. The final product was dried again in vacuum oven at 70 °C to obtain MB₆ NCs in 33% yield.

- 5 The solid state reactions were repeated under different conditions as shown in table 2.

Table 2: reaction conditions for solid state synthesis of MB₆

MCl _x	Molar ratio MCl _x : NaBH ₄	Reaction temperature (°C)	Reaction time (h)	Yield (%)
LaB ₆	1:6	440	23	~ 3%
LaB ₆	1:6.6	440	23	~4.85%
LaB ₆	1:10	380	23	~17.1%
LaB ₆	1:15	400	23	~33.4%
SrB ₆	1:6	440	23	0.5 %
SrB ₆	1:6.6	440	23	~16- 23%
SrB ₆	1:10	440	23	~33%
SrB ₆	1:15	440	23	~65%

- 10 The reactions from table 1 were repeated using SrCl₂, CeCl₃, CaCl₂ and BaCl₂ instead of LaCl₃ which gave similar results.

1.1 Characterization of MB₆ NCs

- The cubic crystal structure (Pm-3m) was confirmed for all studied MB₆ NCs and the XRD patterns are presented in the Figure 1c. The parameters extracted from the Rietveld refinement are shown in Table 3 and in agreement with the literature. (Doebelin, N.; Kleeberg, R. Profex: a graphical user interface for the Rietveld refinement program BGMN. *J. Appl. Crystallogr.* **2015**, *48* (5), 1573-1580) We performed iDPC (Figure 1 f, h) (Integrated Differential Phase contrast) STEM (Scanning Transmission Electron Microscopy) measurements on SrB₆ NCs, and we were able to visualize the B₆ octahedra forming the cubic cages where the M cation

sits. We confirmed this by the simulated iDPC image (Figure 1g). Moreover, the iDPC intensity mapping in the line profile showed different contrast between the top boron and shoulder boron atoms from octahedra. Figures 1e-f show the morphology of the cubic SrB₆ NCs with the average size of 14 ± 6.6 nm.

5

Table 3: MB₆ NCs lattice parameters and crystallite size derived from the Rietveld refinement; * Mackinnon, I. D. R.; Alarco, J. A.; Talbot, P. C. Metal Hexaborides with Sc, Ti or Mn. *MNSMS* 2013, 03 (04), 158-169.

MB ₆ Sample	Crystallite size from Rietveld refinement	α , lattice parameter from Rietveld refinement	α , lattice parameter from ¹⁰ literature*
CaB ₆	4.4 ± 0.2 nm	4.145 Å	4.1514 Å
SrB ₆	6.5 ± 0.1 nm	4.200 Å	4.1953 Å
BaB ₆	1.91 ± 0.03 nm	4.1531 Å	4.2618 Å
LaB ₆	7.4 ± 0.2 nm	4.156 Å	4.1569 Å
CeB ₆	6.2 ± 0.7 nm	4.140 Å	4.1407 Å

- 15 The B-B_{inter-oct} and B-B_{intra-oct} bonds and the M-B₆ interactions were studied with Raman spectroscopy. MB₆ belongs to a cubic Oh group, therefore, all corresponding vibration modes were identified and shown in Figure 1d and Table 4. We noticed a shift from CaB₆ to SrB₆ and BaB₆ of 1280, 1218 and 1139 cm⁻¹ respectively, which we attributed to the variation of the lattice parameters and the NCs' size variation.
- 20 ²⁵T_{2g} and T_{1u} were less affected by the structural and morphological changes in the materials.

Table 4: Raman and FT-IR bands in MB₆ NCs.

	Raman bands	Corresponds to	Reference
5	T _{2g} , 749 ~ 760 cm ⁻¹	scissoring displacement of B atoms in B ₆ octahedra	1
	E _g , 1101 ~ 1131 cm ⁻¹	compressing up and down vibrations in B ₆ octahedra	1
10	A _{1g} , 1216 ~ 1246 cm ⁻¹	stretching of B-B bond	1
	T _{1u} , 191 ~ 206 cm ⁻¹	metal cation with respect to the boron cluster	2
	FT-IR bands		
	590 ~ 630 cm ⁻¹	B-B bending	3,4
15	848 ~ 886 cm ⁻¹	B-OH bending	3,4
	1311 cm ⁻¹	B – O stretching	3,4
	1620 cm ⁻¹	B-OH stretching	3,4
	2400 cm ⁻¹	B-H stretching	3,4
	3200 cm ⁻¹	B-OH stretching	3,4

20 We complemented the Raman measurements with FTIR studies (Figure 3) and we observed bands at 848-886 cm⁻¹, 1620 cm⁻¹ and 3200 cm⁻¹ showing the -OH functionalization, inherited during the vigorous washing steps.

The band at 1311 cm⁻¹ (B-O) also shows that the boron on the surface was oxidized.

25 The bulk LaB₆ didn't show any B-O or B-OH vibration leading to the conclusions that the active polar washing process in combination with high surface area of the NCs were accelerating the oxidation processes. This observation required in-depth investigation, hence, we turned to solid-state NMR spectroscopy, and we used two-dimensional experiments that correlates multiple quantum signals (isotropic lines)

30 with magic angle spinning (MAS) signals. (Figure 2a-e). We first measured the standard bulk LaB₆ and B₂O₃ (Figure 2a, b) and compared it with the measurement for our synthesized (and washed) LaB₆ and SrB₆ NCs. We learned that indeed, B₂O₃

was present in our materials while the signal correlated to the MB₆ was as expected from the comparison with the bulk LaB₆. The annular dark-field scanning electron microscopy (HAADF-STEM) revealed that the B₂O₃ is an amorphous shell around our NCs.

5

1.2 Surface functionalization of surface activated SrB₆ and LaB₆ NCs

For the surface modification of SrB₆ nanocrystals, TFSI stabilized SrB₆ NC solutions were prepared using N-Methyl formamide (NMF), Formamide, and dimethylsulfoxide (DMSO) as polar solvents. 25 mg (0.19 mmol) of solid state synthesized SrB₆ NCs was added to the solution containing 20 mg (0.07 mmol) of TFSI in 1 mL of polar solvent. The solution mixture was stirred overnight at 90 °C to obtain a colloidal dispersion of SrB₆ NCs. 0.2 mL of toluene was used as anti-solvent to wash the nanocrystals then centrifugation at 5000 RPM for 2 minutes. Washing was performed two times.

15

For the preparation of TFSI stabilized LaB₆ NCs, 20 mg of LaB₆ NCs (0.098 mmol) was added to 20 mg (0.07 mmol) of TFSI in 1 mL DMSO. The solution mixture was stirred overnight at 90 °C to obtain colloidal dispersion of LaB₆ NCs. A mild washing (1x times) step was adopted by only using 0.2 mL of acetone as anti-solvent and centrifuged at 5000 RPM for 3 minutes. A colloidal dispersion was formed (comparison before (Figure 4A) and after (Figure 4B) reaction).

20

LaB₆ NCs show good stability with TFSI ligands in DMSO (C=20 mg/mL) for around three days while the SrB₆ NCs proved increased stability in NMF up to 2 months (C=25 mg/mL).

25

The reaction described above was repeated by dissolving 20 mg of Boron triiodide (BI₃) in NMF (1 mL), 30 mg BI₃ in MFA (1 mL) or NOBF₄ in NMF (1 mL). 20 mg of SrB₆ NCs was added to these solutions and the mixtures were stirred at 90 °C for 16 h. A colloidal dispersion was formed (comparison before (Figure 4C) and after (Figure 4D) reaction). The colloidal dispersion of SrB₆ NCs was centrifuged at 5000 RPM for 3 minutes without any anti-solvent due to limited stability. The washed precipitate can be redispersed in NMF.

30

The reaction described above was repeated by dissolving 30 mg of *tert*-butylamine (BTBA) in MFA (1 mL). 20 mg of SrB₆ NCs was added to this solution and stirred at 90 °C for 16 h. No colloidal dispersion was formed (comparison before (Figure 4E) and after (Figure 4F) reaction).

It can be concluded from Figure 4 that surface functionalization of MB₆ NCs was successful for boron halides and sulfonimides, but not for tertiary amines, such as BTBA.

10

1.3 Ligand exchange of surface functionalized SrB₆ and LaB₆ NCs

The SrB₆ NCs surface functionalized with BI₃ ligands obtained with the method described in section 1.2 was dispersed in DMSO (C= 25 mg/mL) to perform the ligand exchange. 1M oleylamine in hexane (1 mL) was added to SrB₆ NCs dispersed in DMSO, the biphasic mixture was allowed to stir for 2 hours. Once the SrB₆ NC moved from the polar solvent phase to the non-polar hexane phase, the top part (SrB₆ - olam in hexane) was separated and washed with 0.2 mL of ethanol (2x wash). Washed SrB₆ NCs were finally redispersed in toluene.

The LaB₆ NC precipitate was dispersed in DMSO, and further ligand exchange was done on the LaB₆ NCs in DMSO. The same procedure of ligand exchange (as mentioned in SrB₆ NCs) was adopted for LaB₆ NCs. Washing was performed with 0.05 mL of ethanol (1x wash). The washed LaB₆ NCs was finally dispersed in toluene.

1.4 Characterization of surface-functionalized SrB₆ and LaB₆ NCs

The XRD pattern before and after surface functionalization are shown in Figure 5a (SrB₆ NCs) and Figure 5b (LaB₆ NCs). In both cases the structure and morphology are maintained for the BI₃ treatment.

SEM images of SrB₆ NCs before (Figure 5c) and after (Figure 5d) surface modification with BI₃ and subsequent replacement with OLA ligands, confirmed successful surface modification. A transmission electron microscopy (TEM) image of SrB₆ OLA NCs confirms the cubic shape (Figure 5d, right inset). Particle size

distribution for SrB₆/OLA NCs shows the size distribution is maintained (around 10-12 nm in average; Figure 5e).

5 These results confirm that ink compositions comprising LaB₆ and SrB₆ NCs could be successfully prepared comprising BI₃, TFSI and OLA ligands allowing colloiddally stable dispersions in both polar and nonpolar solvents.

Example 2: Surface functionalization of nickel borides (Ni₃B) – reference example

10 The reaction described in Example 1.2 was repeated by dissolving 8.69 mg of Borane Tert-butylamine in DMSO (1 mL) and adding 10 mg of Ni₃B NCs to this solution and stirred at 90 °C for 16 h. A colloidal dispersion was formed (comparison before (left-hand panel of Figure 7A) and after the reaction (right-hand panel of Figure 6A)).

15 The reaction described in Example 1.2 was repeated by dissolving 30 mg of TFSI in MFA (1 mL) and adding 20 mg of Ni₃B NCs to this solution and stirred at 90 °C for 16 h. No colloidal dispersion was formed (comparison before (Figure 6B) and after (Figure 6C) reaction).

20 The reaction described above was repeated by dissolving 30 mg BI₃ in MFA (1 mL) and adding 20 mg of Ni₃B NCs was added to this solution and stirred at 90 °C for 16 h. No colloidal dispersion was formed (comparison before (Figure 6D) and after (Figure 6E) reaction).

25 It can be concluded that tertiary amines were suitable for surface functionalization of Ni₃B, but not metal halides (BI₃) or sulfonimides (TFSI). This is contrary to metal hexaborides, wherein metal halides and sulfonimides were both successful ligands, but not tertiary amines.

30 **Example 3: Thin film preparation using blade coating on Si/SiO and sapphire wafers**

SrB₆ NCs colloidal dispersions using BI₃ or BF₄ as surface ligand were prepared using the method described in Example 1.2. The concentration of NCs was

maintained at 50 mg/ml in the colloidal solution. The substrate chosen for coating were Si/SiO and sapphire wafers. The substrates were cut in to 1x1 cm dimensions and cleaned thoroughly using deionized water, then heated up to 55 °C in an acetone bath followed by acetone wash. Further the substrates were immersed in isopropanol (IPA) and sonicated for 20 minutes. Finally, the substrates are washed with fresh IPA and eventually are dried by blowing compressed nitrogen. The etching was performed on clean silicon wafers using ammonium bifluoride. The etching solution was applied on the surface of the silicon and left in the air for about an hour and further cleaned with DI water and dried in the oven. The dried substrates were subjected to UV ozone treatment for 20 minutes.

Blade coating was performed on the treated substrates at 90 °C and 20 µl of NC solution was used per coat, using a Zehntner ZAA 2300 automatic film applicator consisting of a heating surface. A motorized applicator was attached to the heating station. The substrate to be coated was placed between the hot plate (set to 90 °C) and the blade, the colloidal ink was dropped on the substrate (~ 20 µl) and waited up to a minute until the evaporation of the solvent from the ink was observed (by just visual appearance of vaporizing solvent). At this point the blade was moved on the substrate (25 mm/sec speed) with the blade height of 0.4 – 0.8 cm from the surface of the substrate. The excess solvent gets pushed from the surface of the substrate, then annealed at 90 °C until all the solvent evaporates, and film is observed on the substrate.

Subsequently, the coated substrates were annealed inside the glovebox on a hot plate at 350 °C for 2 h inside the glove box under N₂ atmosphere.

25

Example 4: Hardness measurements

The thin films prepared with the method according to Example 3 were subjected to hardness measurements as described below.

Hardness measurements were performed on FT-I04 Femto-indenter manufactured by Femto tools consisting of high-resolution bi-axial force sensor, elastic moduli, and hardness were measured under integrated continuous stiffness mode, and applied force range was between – 400 µN to 400 µN. The piezo sensor was equipped with a Berkovich tip. The measurements were performed using CSM

30

mode (continuous stiffness measurement). During CSM, an oscillation force with a frequency of 200 Hz is applied by the tip. Each oscillation emphasizes the loading and unloading process, resulting in better accuracy of contact stiffness and area function.

5 The results are shown in Figure 7. The thin films showed hardness of around 10 GPa ($\text{SrB}_6\text{-BI}_3$; Figure 7a) and reduced moduli of 147 GPa ($\text{SrB}_6\text{-BI}_3$; Figure 7b). The experiments were repeated multiple times and an average hardness of around 10 GPa ($\text{SrB}_6\text{-BI}_3$) and 5 GPa ($\text{SrB}_6\text{-BF}_4$) and a Young's modulus of about 190 GPa ($\text{SrB}_6\text{-BI}_3$) or 170 GPa ($\text{SrB}_6\text{-BF}_4$) was obtained on Si/SiO wafers (Figure 7c-d) and a
10 hardness of around 6 GPa ($\text{SrB}_6\text{-BF}_4$) and a Young's modulus of about 300 GPa ($\text{SrB}_6\text{-BF}_4$) on sapphire wafers (Figures 7E-H).

The experiments were conducted at different depths, varying from below 0.3 μm to up to 1.2 μm . The results were consistent and confirm that the results reflect the hardness and Young modulus of the layer, and not the substrate.

15 As additional control experiment, the hardness and Young modulus of the uncoated silicon wafer was determined at 12 GPa and 180 GPa. The hardness values obtained for the $\text{SrB}_6\text{-BI}_3$ and $\text{SrB}_6\text{-BF}_4$ thin films were well below 12 GPa, confirming that our measurements are indeed reflective of the thin films and not the substrate.

20

Example 5: Solid state Synthesis of MB_2 (M=Hf)

Hafnium tetrachloride was reacted with sodium borohydride at different molar ratios, from 1:2 to 1:6 (HfCl_4 : NaBH_4) at 440 °C for 23 hours. Both the precursors were added to a 25 ml round bottom flask inside the glove box, under N_2 atmosphere.
25 The precursors in the round bottom flask were moved to Argon connected Schlenk line and the reactions were performed at 440 °C. The reaction precursors turn brown at the beginning of 300 °C and soon turns black at 360 °C. After 23 hours, the product is washed with deionized water and 0.5 M HCl to wash the byproducts formed during the reaction. As shown in Figure 8a The reaction containing Hf: B: 1:2 was not
30 successful in producing HfB_2 , but at molar ratio of 1:4 and 1:6, nanocrystals of HfB_2 were observed. Reactions performed at 300 °C did not yield HfB_2 NCs.

5.2 Surface functionalization of surface activated HfB_2 NCs

Further HfB₂ NCs (nanopowders) produced using 1:4 ratio of Hf:B, were treated with boron triiodide (BI₃: 0.025 mmol) in dimethyl formamide (DMF) at 60 °C. Figure 8b shows the stable HfB₂ NCs (0.024 mmol) in DMF after 48 hrs.

5

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30

Claims

1. An ink composition for depositing a coating on a substrate, comprising a colloidal dispersion of metal boride nanocrystals (NCs) in a liquid medium, wherein
5 said metal boride NCs are selected from metal hexaborides (MB_6) and metal diborides (MB_2), and wherein said metal boride NCs are at least partly coated with a dispersing aid, wherein said dispersing aid is a ligand comprising a boron-binding moiety and wherein said metal boride NCs are present in said ink composition in a concentration of at least 10 mg/mL.
- 10 2. The ink composition according to claim 1, wherein said colloidal dispersion is essentially stable for 24 h or more, preferably wherein the concentration of said metal boride NCs dispersed in said liquid medium after 24 h deviates 10% or less from the initial concentration of said metal boride NCs dispersed in said liquid medium.
- 15 3. The ink composition according to any of the preceding claims, wherein said boron binding moiety comprises:
 - a boron atom, preferably a borane, a borate or a boron halide, more preferably a borane selected from dodecaborate and *closo*- B_6H_6 or a boron halide selected from boron iodide and boron chloride; or
 - 20 - a nitrogen atom, preferably a sulfonimide or a fatty amine, more preferably bis(trifluoromethane)sulfonimide or oleylamine; or wherein said ligand comprises an alkyl moiety or an alkenyl moiety, preferably an alkyl moiety comprising a C_6 - C_{21} carbon chain.
- 25 4. The ink composition according to any one of the preceding claims wherein said metal boride NCs are present in a concentration of at least at least 20 mg/mL, preferably at least 30 mg/mL, more preferably at least 40 mg/mL, most preferably at least 50 mg/mL.
- 30 5. The ink composition according to any one of the preceding claims, wherein said metal boride NCs are MB_6 NCs, preferably wherein said metal boride NCs are MB_6 NCs selected from lanthanum hexaboride (LaB_6), strontium hexaboride (SrB_6), calcium hexaboride (CaB_6), cerium hexaboride (CeB_6) and barium hexaboride (BaB_6).

6. A solid composition suitable for preparing an ink composition according to any one of claims 1 to 5, comprising metal boride NCs at least partly coated with a dispersing aid, wherein said metal boride NCs are selected from MB₆ NCs and MB₂ NCs and wherein said dispersing aid is a ligand comprising a boron-binding moiety.
7. A method for coating an object comprising, providing an object with a coating of an ink composition according to any one of claims 1-5 and allowing said coating to dry.
8. The method according to claim 7, wherein said coating is allowed to dry at a temperature of at most 90 °C, more preferably at most 50 °C, in particular at most 30 °C.
9. A coating of a dried ink composition according to any one of claims 1-5.
10. An object comprising a coating according to claim 9.
11. The object according to claim 10, wherein said object comprises a substrate coated with said coating, wherein said substrate is a flexible substrate, a textural substrate, or a substrate having a melting point of below 100 °C, preferably a melting point of between about 20 °C and about 100 °C.
12. The object according to claim 10 or 11, wherein said coating has a thickness of between about 200 nm and about 5 μm and/or wherein said coating has a hardness of at least 150 MPa, preferably at least 5 GPa and/or wherein said coating has a Young's modulus of at least 20 GPa, preferably at least 150 GPa.
13. A method for preparing an ink composition according to any one of claims 1 to 5 comprising:
- (i) providing metal boride NCs, wherein said metal boride is selected from MB₆ NCs and/or MB₂ NCs;
 - (ii) subjecting the metal boride NC's to surface activation to obtain surface-activated metal boride NCs; and
 - (iii) contacting the surface-activated metal boride NC's with a solution of a dispersing aid or a precursor thereof, in a polar liquid medium, wherein said dispersing aid or precursor thereof is a ligand comprising a boron-binding moiety to obtain an ink composition comprising metal boride NC's at least substantially colloidally dispersed therein.

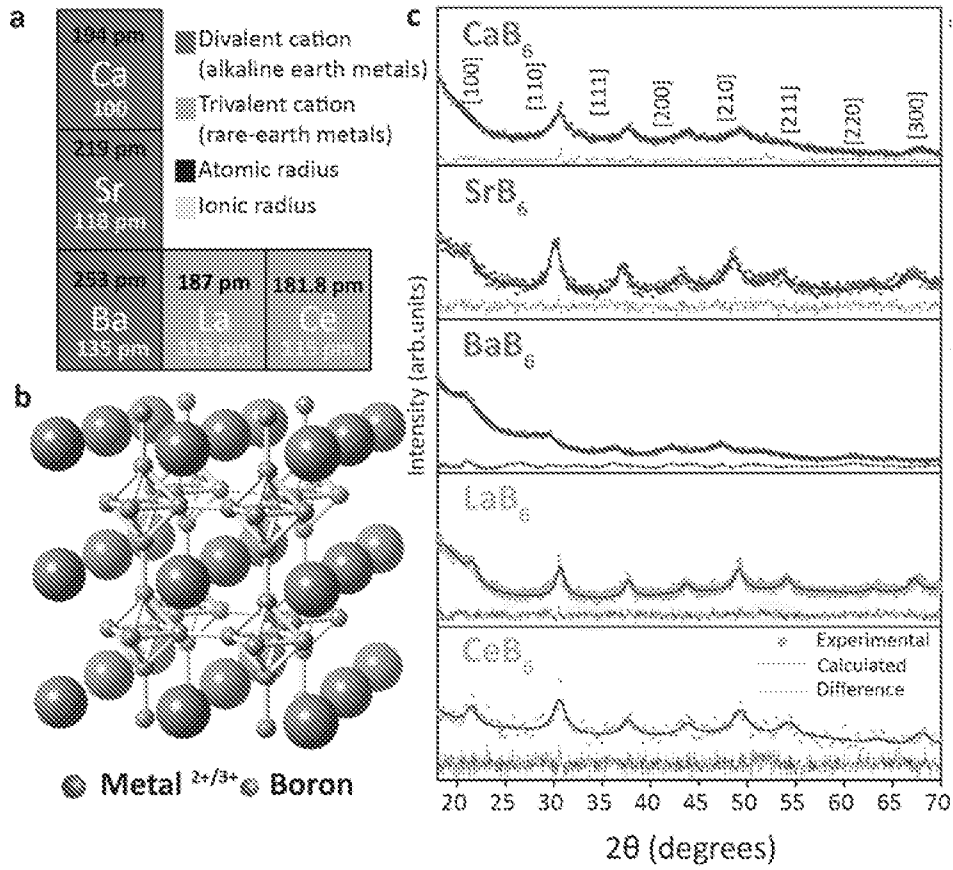
14. The method according to claim 13, wherein said boron binding moiety comprises:

- a boron atom, preferably a borane or a boron halide, more preferably a borane selected from dodecaborate and *closo*-B₆H₆, a borate or a boron halide selected from boron iodide and boron chloride; or
- a nitrogen atom, preferably a sulfonimide, more preferably bis(trifluoromethane)sulfonimide or a fatty amine, more preferably oleylamine; or wherein said ligand comprises an alkyl moiety or an alkenyl moiety, preferably an alkyl moiety comprising a C₆-C₂₁ carbon chain.

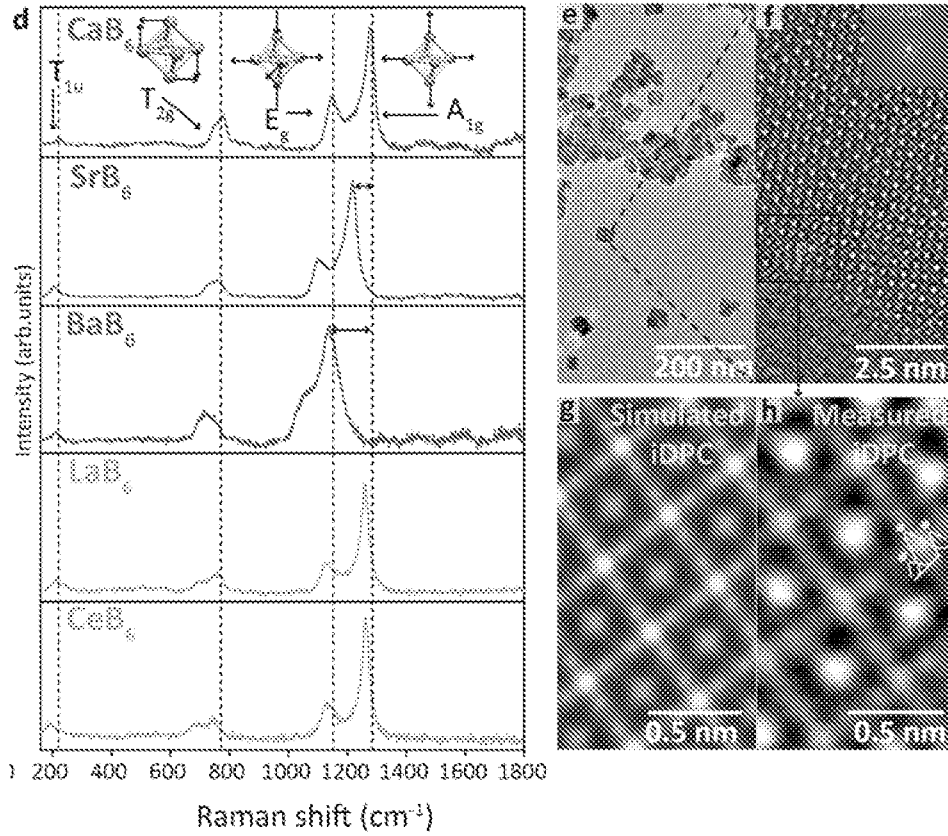
- 10 15. The method according to claim 13 or 14, further comprising
- (iv) contacting the ink composition obtained in step (iii) with a solution of a second dispersing aid or a precursor thereof, wherein said second dispersing aid or precursor thereof is a ligand comprising a boron-binding moiety in a nonpolar liquid medium to form a biphasic system; and
- 15 (v) allowing formation of metal borides NCs at least partly coated with said second dispersing aids to obtain an ink composition comprising a colloidal dispersion of metal boride NCs at least partly coated with said second dispersing aids in a nonpolar liquid medium.

16. The method according to claim 15, wherein said second dispersing aid
- 20 comprises a fatty amine or a fatty acid, preferably oleylamine.

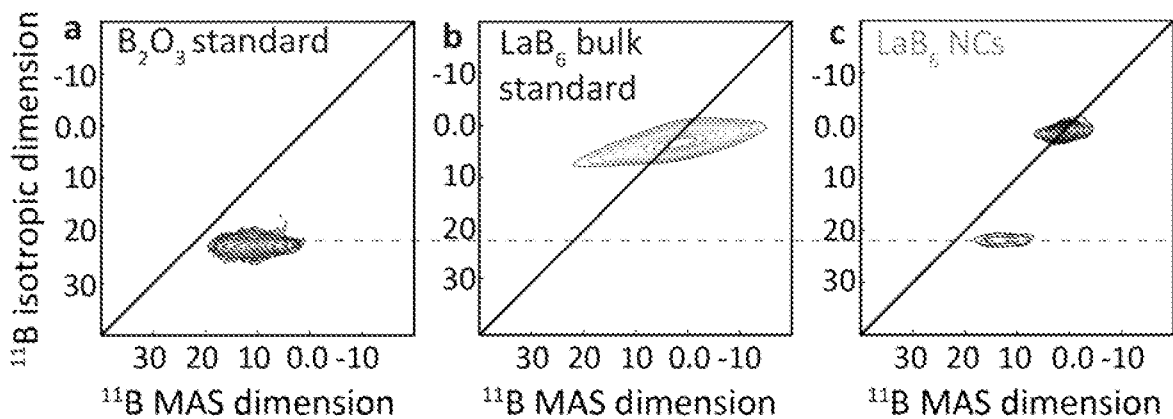
Figures 1 A-C



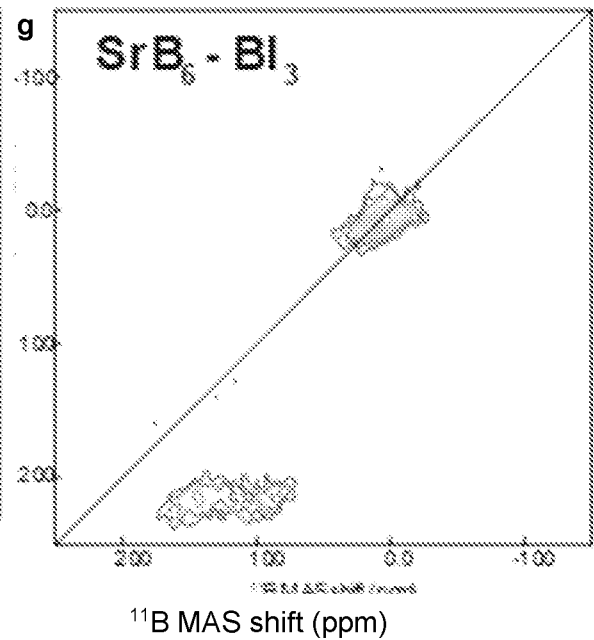
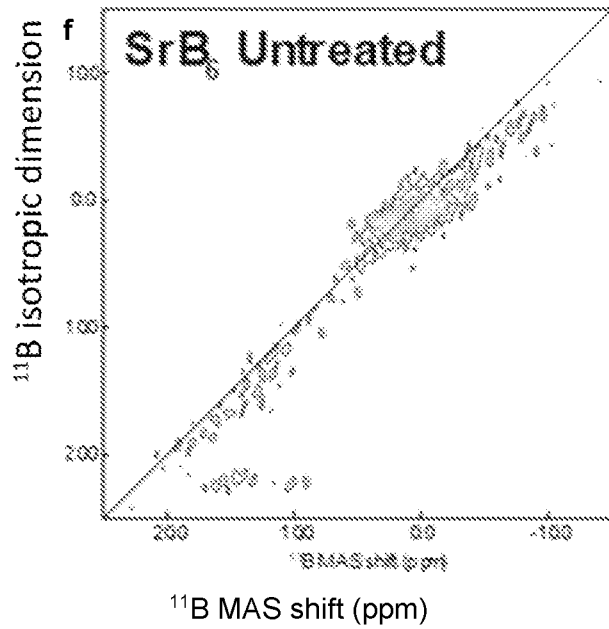
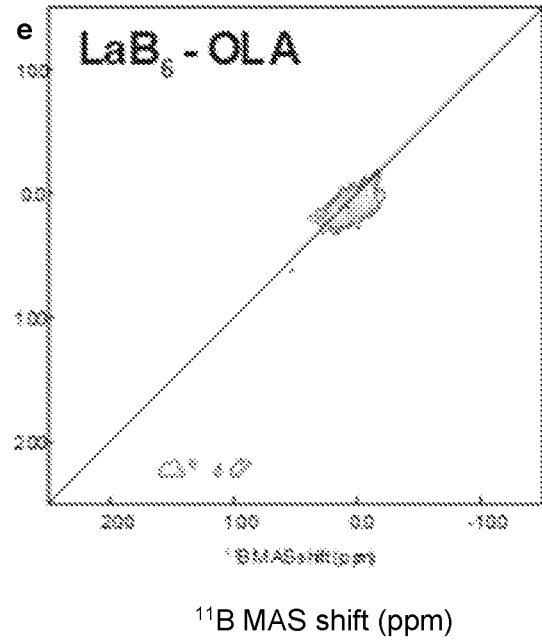
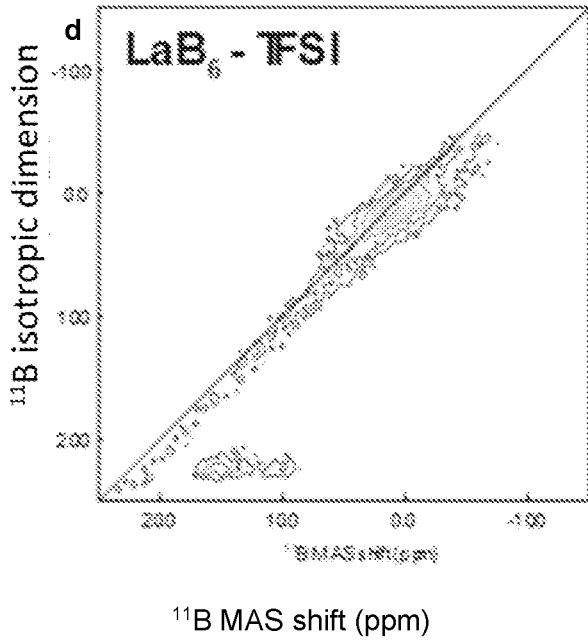
Figures 1 D-H



Figures 2 A-C



Figures 2 D-G



Figures 2 H-I

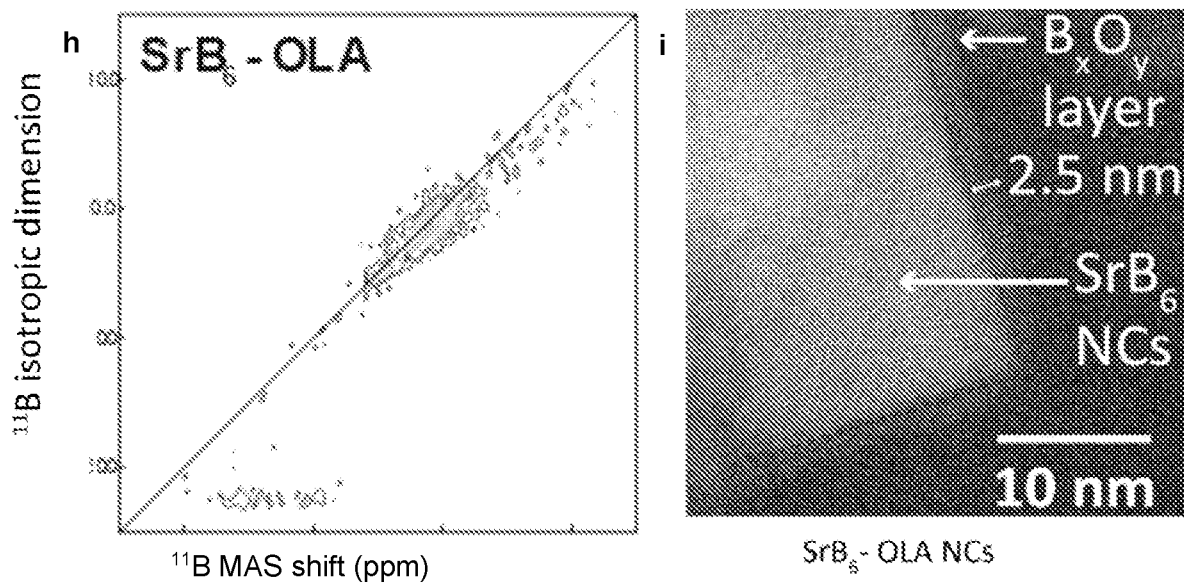
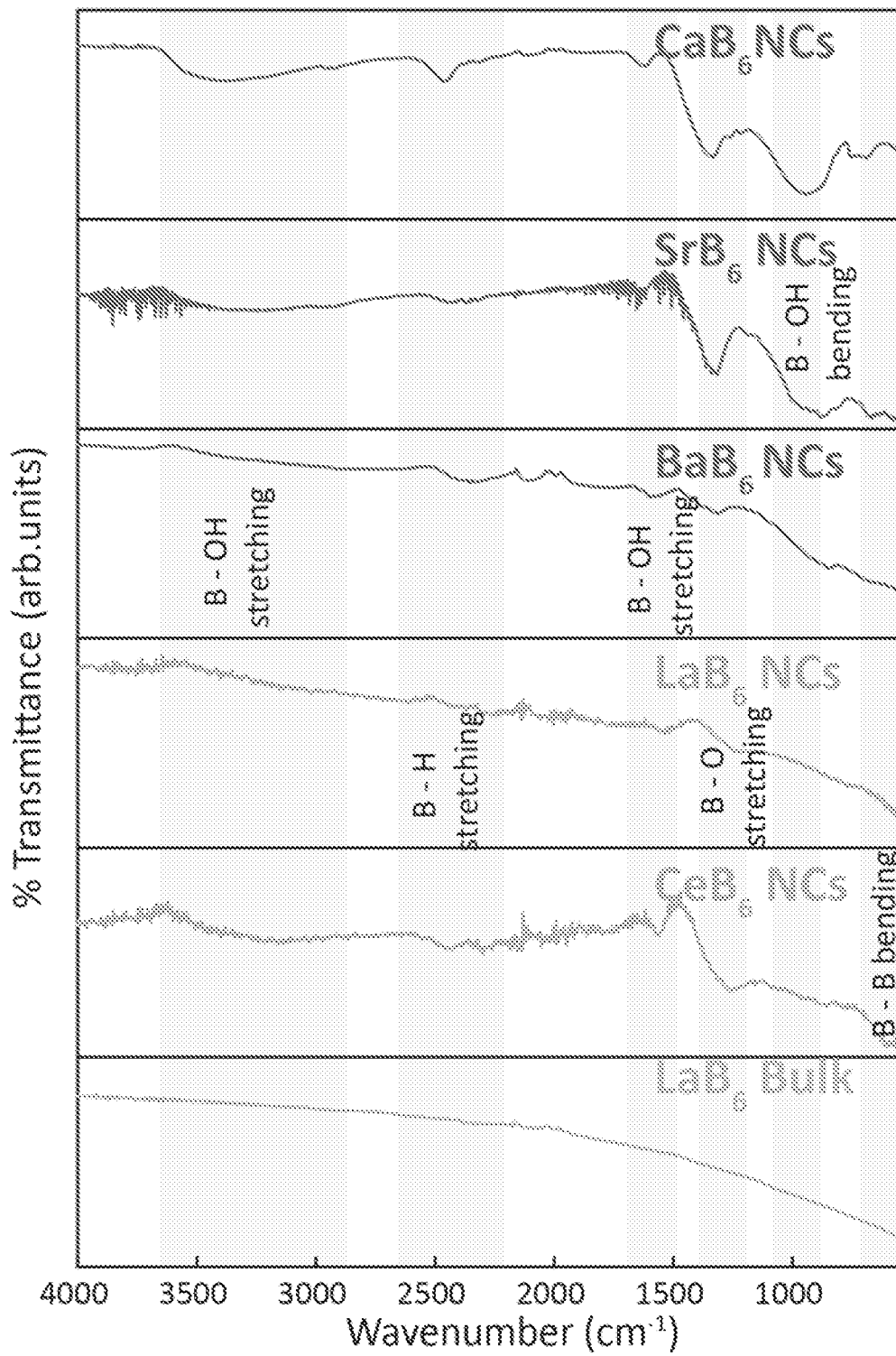
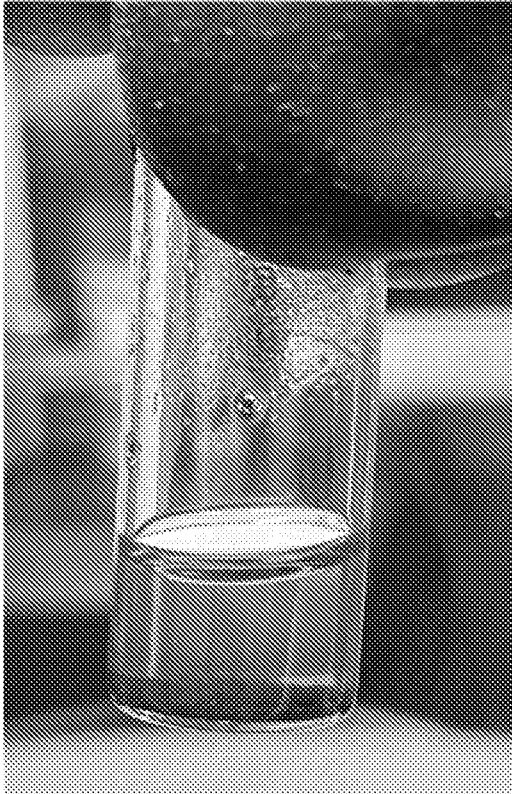


Figure 3

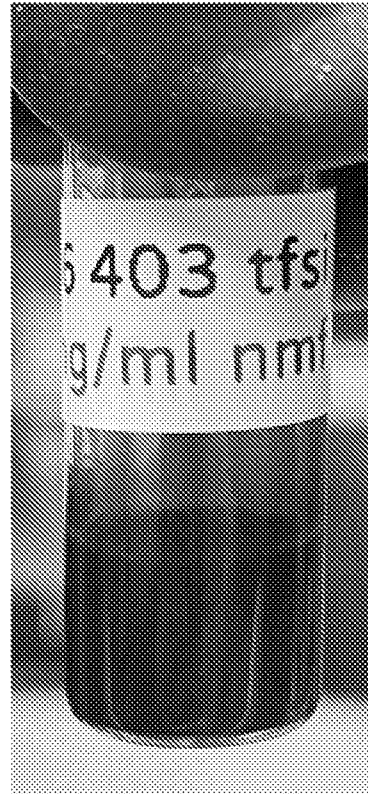


Figures 4 A-D

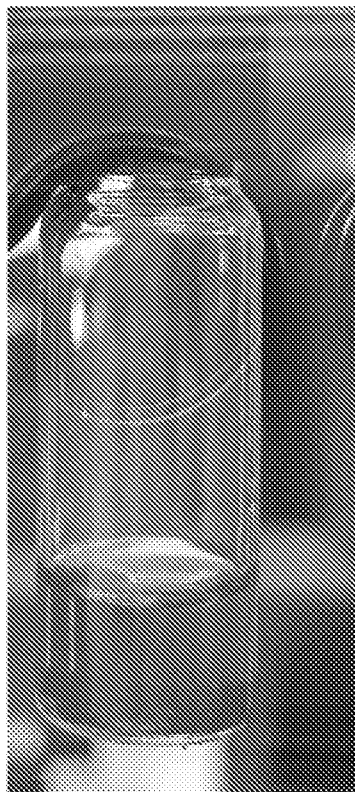
A



B



C



D

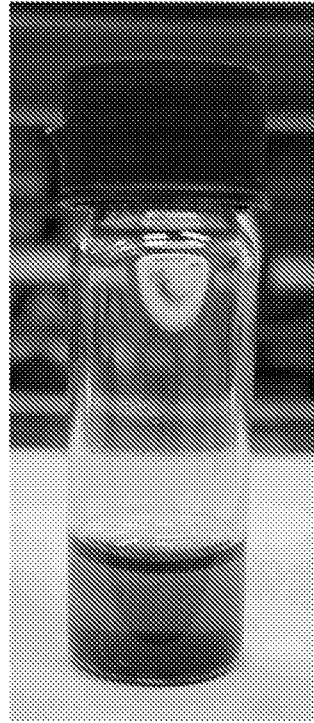


Figures 4 E-F

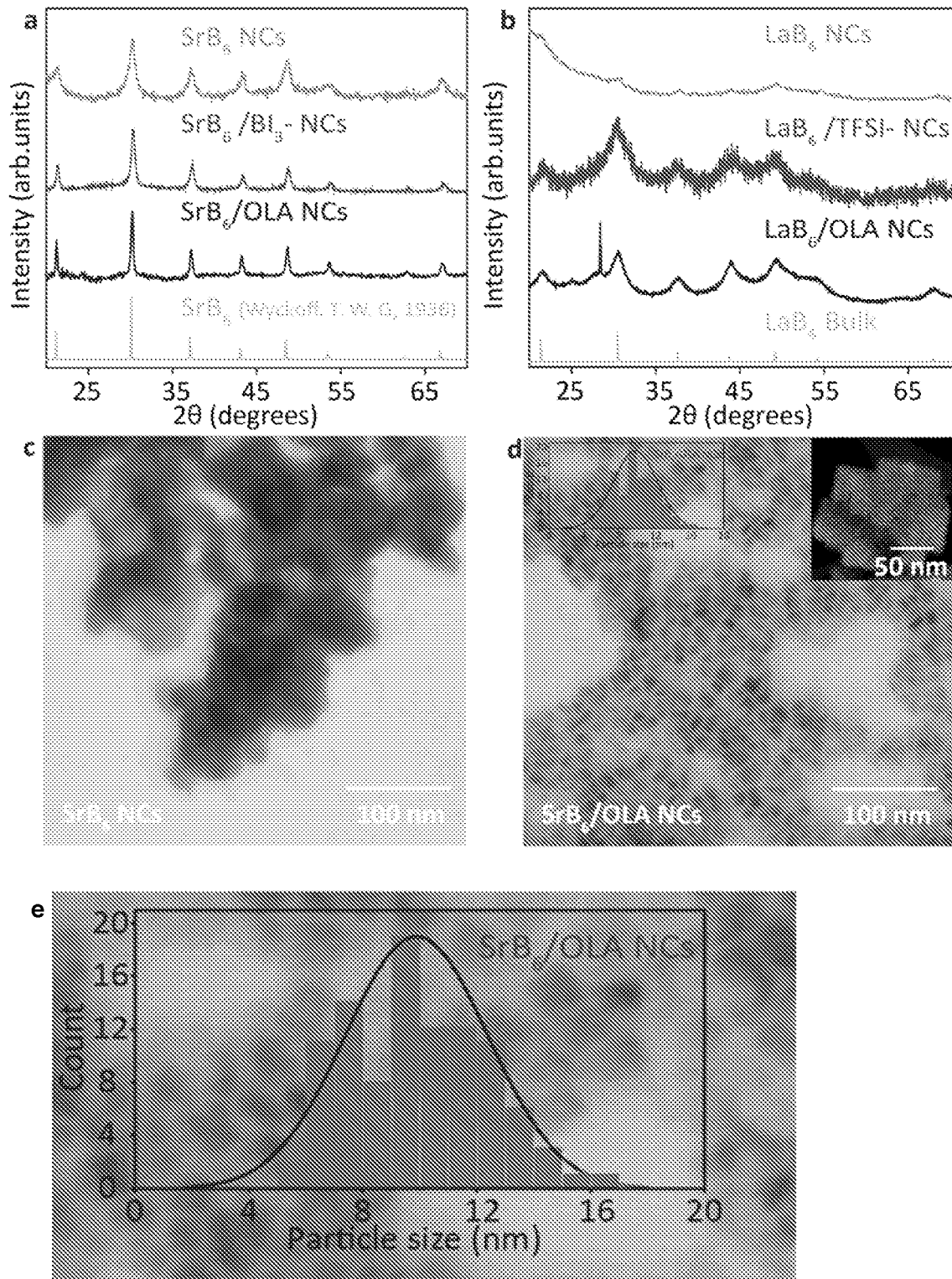
E



F

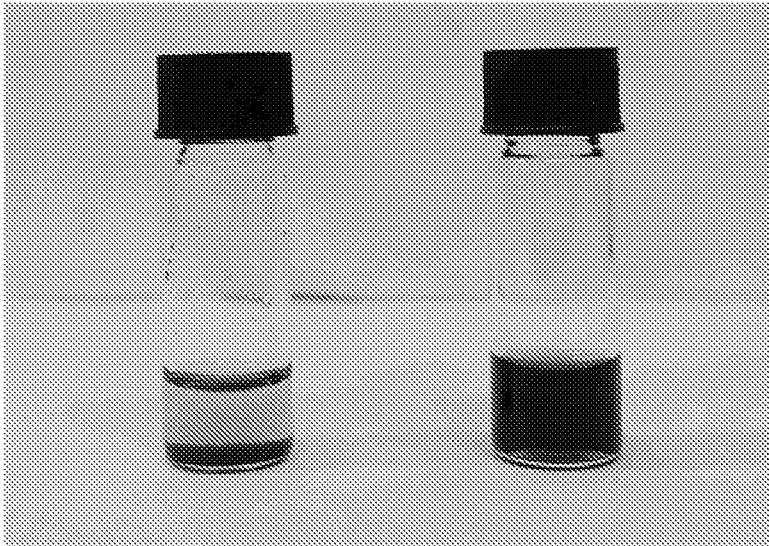


Figures 5 A-E

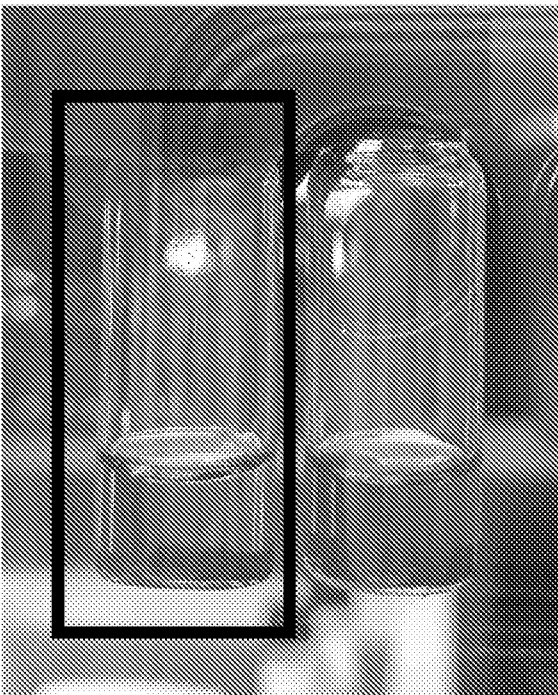


Figures 6 A-C

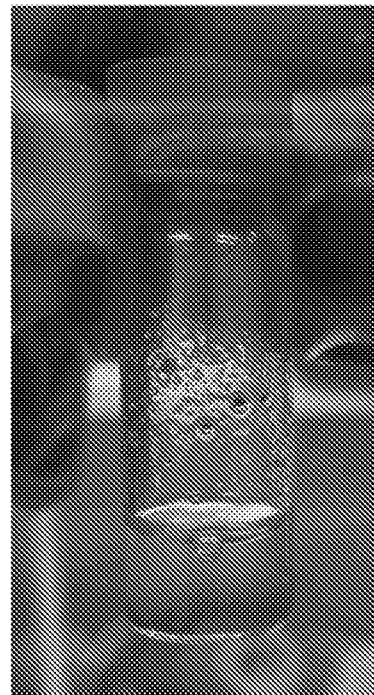
A



B

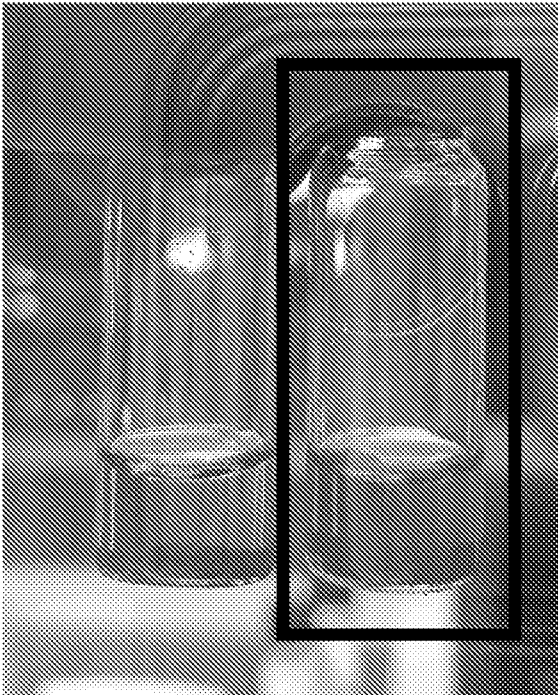


C

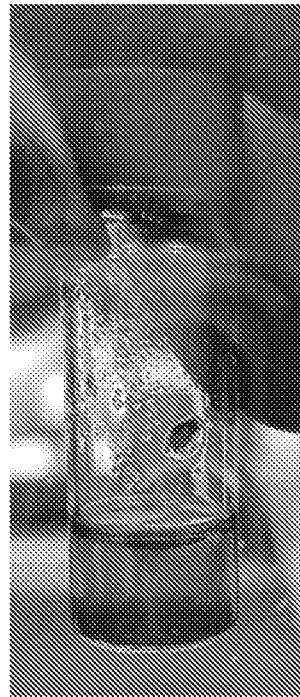


Figures 6 D-E

D



E



Figures 7 A-B

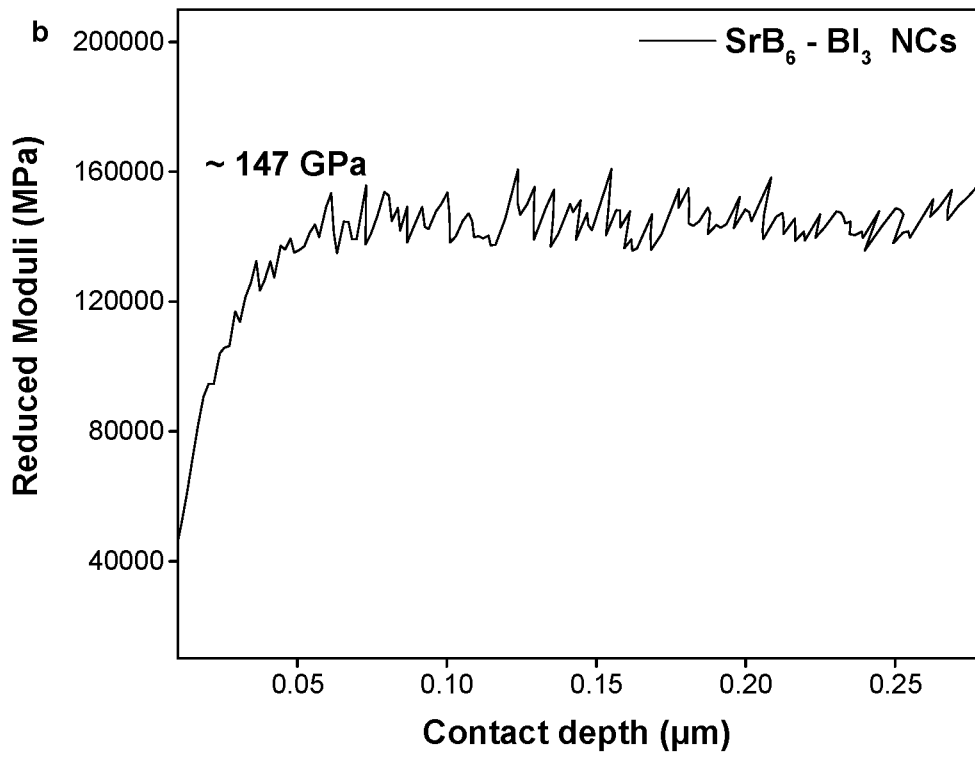
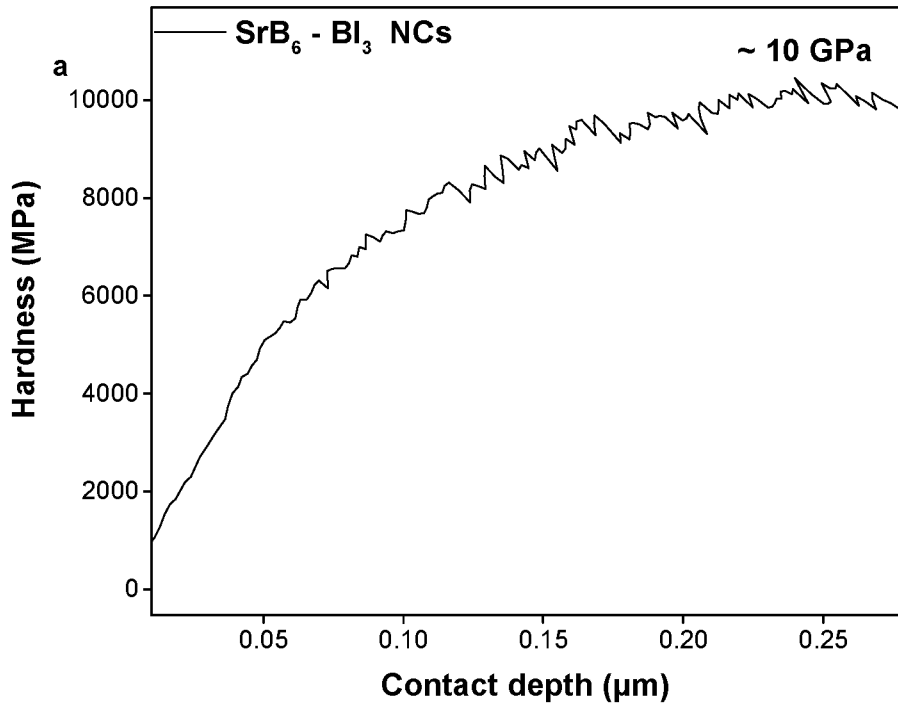


Figure 7 C-D

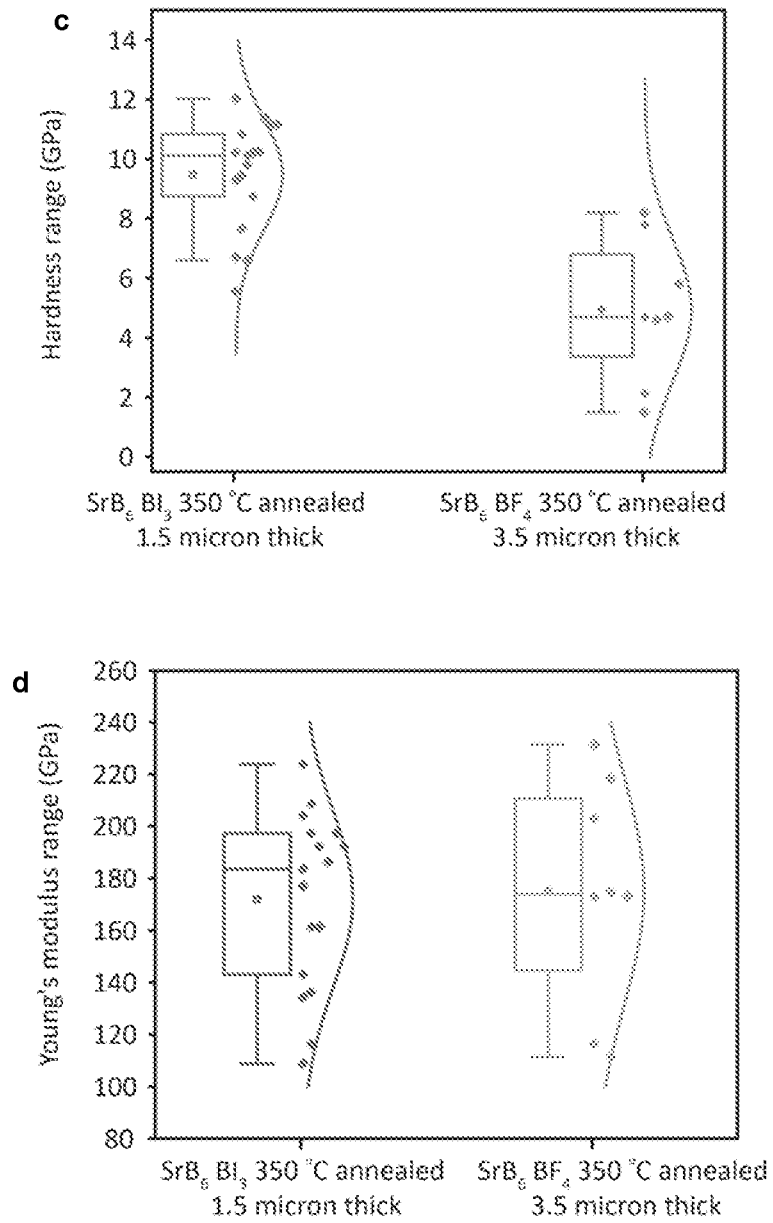
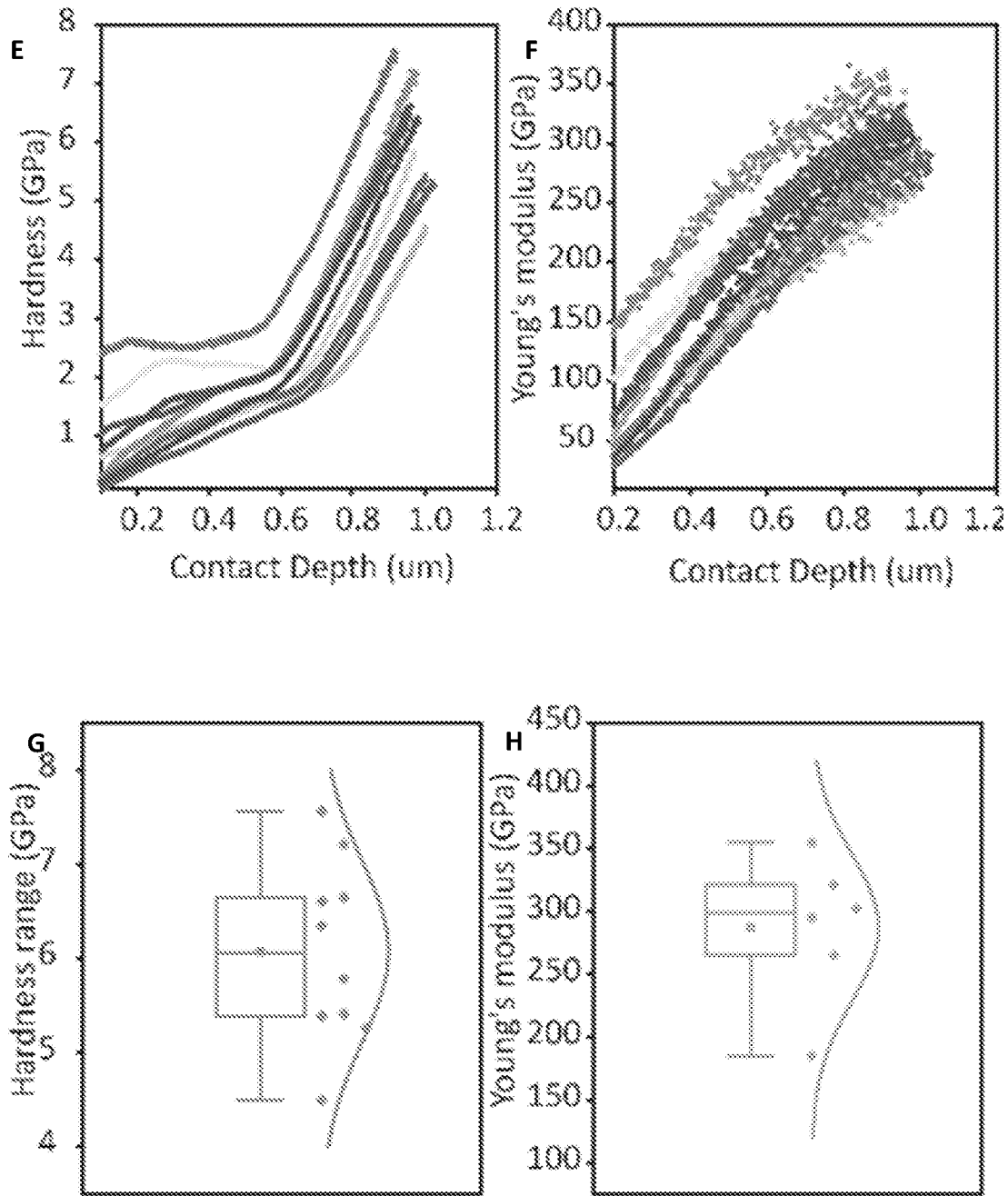
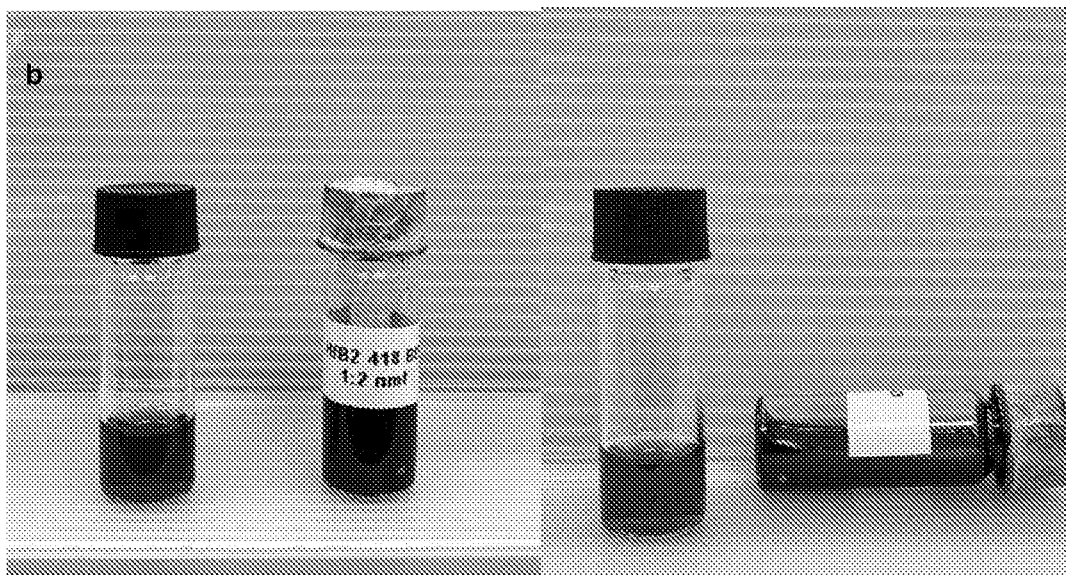
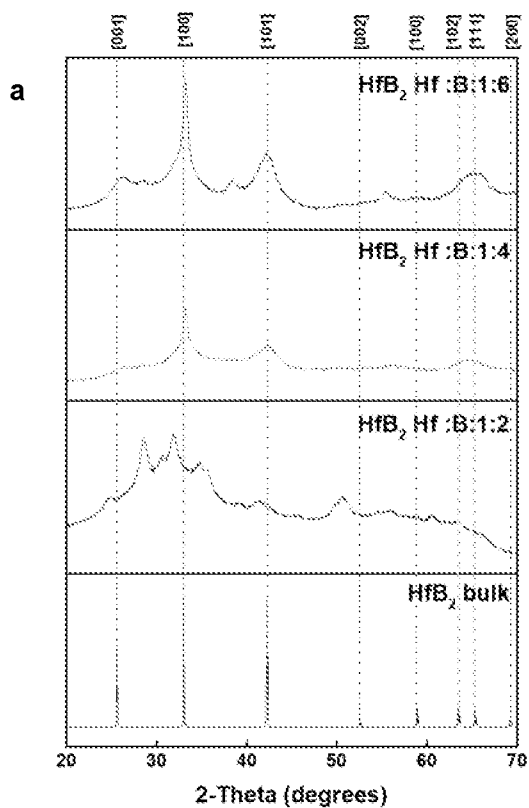


Figure 7 E-H



SrB₆ - BF₄ Sapphire Hardness and Young's Modulus range

Figure 8



INTERNATIONAL SEARCH REPORT

International application No PCT/NL2024/050513

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09D11/037 C09D11/03 C09D11/033 C09D1/00 C09D5/08
 C09D7/20 C09D7/63

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)
 C09D

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/029121 A1 (HAMMERMANN MARKUS [DE] ET AL) 29 January 2009 (2009-01-29) claims 1-4 + 15 + 26-33; par. 199 + 203-204 + 216-219 + 229 -----	1 - 16
X	SOPHIE CARENCO ET AL: "Nanoscaled Metal Borides and Phosphides: Recent Developments and Perspectives", CHEMICAL REVIEWS, vol. 113, no. 10, 9 October 2013 (2013-10-09), pages 7981-8065, XP055384308, US ISSN: 0009-2665, DOI: 10.1021/cr400020d	6
A	chapters 6.2.2 + 6.4 ----- - / - -	1 - 5, 7 - 15

Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 4 November 2024	Date of mailing of the international search report 18/11/2024
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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 von Zitzewitz, A
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INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2024/050513

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHLOE GROOME ET AL: "Effects of Size and Structural Defects on the Vibrational Properties of Lanthanum Hexaboride Nanocrystals", ACS OMEGA, vol. 2, no. 5, 23 May 2017 (2017-05-23), pages 2248-2254, XP055459600, US ISSN: 2470-1343, DOI: 10.1021/acsomega.7b00263 cited in the application	6
A	introduction -----	1-5,7-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2024/050513

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		WO 2007107407 A1	27-09-2007
