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(54) Title: ONE-POT PROCESS FOR PREPARING LUMINESCENT GERMANIUM NANOPARTICLES

(57) Abstract: A process for preparing blue luminescent germanium nanoparticles comprising the following steps (a) reacting a mixture containing (1) at least one germanium (IV) -alkoxide, (2) at least one organosilane and/or organosiloxane containing at least one Si-H group per molecule in at least one hydrocarbon solvent; and (3) a catalytic amount of Lewis acid catalyst under stirring under inert atmosphere at a temperature in the range of from 80 °C to 300 °C, wherein the molar ratio of germanium (IV) -alkoxide to Si-H groups is in a range of from 1:4 to 1:10; and (b) stabilizing germanium nanoparticles by adding at least one surface bonding agent or by exposure to the ambient air.



One-pot process for preparing luminescent germanium nanoparticles

The present invention relates to a process for preparing blue
5 luminescent germanium nanoparticles comprising the following steps:

- (a) reacting a mixture containing
- (1) at least one germanium(IV)-alkoxide;
 - (2) at least one organosilane and/or organosiloxane
 - 10 containing at least one Si-H group per molecule in at least one hydrocarbon solvent; and
 - (3) a catalytic amount of Lewis acid catalyst according to formula (V)



wherein

each R^5 is independently selected from substituted or unsubstituted aromatic radicals having from 5 to 14 carbon
20 atoms;

X is a halogen atom;

x is 1, 2, or 3; and

y is 0, 1 or 2;

with the proviso that $x + y = 3$, and the further proviso

25 that the catalyst comprises at least one electron withdrawing group;

under stirring under inert atmosphere at a temperature in the range of from 80 °C to 300 °C, wherein the molar ratio of germanium(IV)-alkoxide to Si-H groups is in a range of
30 from 1:4 to 1:10; and

- (b) stabilizing germanium nanoparticles by adding at least one surface bonding agent or by exposure to the ambient air.

Background of the Invention

Semiconductor nanoparticles also called quantum dots (QDs) are single nanosized objects containing a semiconductor core consisting of hundreds to thousands of atoms in the size
5 ranging from about 1 nm to about 10 nm in radius, which is comparable to the Bohr exciton radius. Semiconductor nanoparticles of the size comparable to the Bohr exciton radius exhibit new electronic properties related to the so-called quantum confinement effect. Such nanoparticles showed unusual
10 optical properties such as blue shift of the band edge light absorption and luminescence emission with decreasing particle size. Semiconductor QDs are an exciting new class of materials with a wide range of applications from medical to optoelectronics. Most of the currently developed and utilized
15 in commercial applications QDs are composed from Group II-VI, III-V and IV-VI semiconductors and contain toxic heavy metals such as lead, mercury, cadmium and arsenic. The presence of these toxic elements puts in question the wide applications of QDs. Quantum dots are very small semiconductor particles, only
20 several nanometers in size, so small that their optical and electronic properties differ from those of larger particles. Many types of quantum dots will emit light of specific frequencies when electricity or light is applied to them, and these frequencies can be precisely tuned by changing the dots'
25 size, shape and material.

Silicon based quantum dots and their sister germanium quantum dots (GeQDs) have become a new, non-toxic alternative to heavy metals containing QDs. GeQDs called also germanium nanocrystals
30 (GeNCs) or germanium nano-particles (GeNPs) were discovered 35 years ago, in 1982 by Hayashi et al.¹ Germanium is especially appealing compared to silicon due to the higher electron and hole mobility, larger dielectric constant (16 vs 11.9),

narrower bulk band gap (0.67 eV at 300 K), implying the possible tuning of light emission over as much as 3.3 eV, corresponding to wavelengths from the near-UV to the near-IR (NIR). The Bohr exciton radius for germanium is calculated to be 24.3 nm, which is much larger than the well-known silicon Bohr radius (4.5 nm). Larger Bohr radius will impart stronger, more easily identified effects of quantum confinement for germanium than silicon for the same size nanocrystals.²

Since germanium is the element directly neighboring with silicon within the same 14th group of the Periodic Table, a similarity might be expected between chemistries of these elements. Indeed, most methods used to prepare GeQDs involve the same reactions, which were used to prepare Si quantum dots.^{2, 3}

Reduction of germanium halides GeX_4 , where $\text{X} = \text{Cl}, \text{Br}, \text{J}$, with various hydrides was used extensively for preparation of GeQDs.^{4, 5} Highly crystalline 5 nm GeQDs were prepared by simple reaction of GeCl_4 / PVP (polyvinylpyrrolidone) in ethylene glycol with NaBH_4 at RT. The formed GeQDs were separated by centrifugation after 30 min of reaction. PVP coated GeQDs were re-dispersed in water, ethanol or acetonitrile. Tilley et al. used a similar process to the synthesis of GeQDs, which were subsequently passivated by hydrogermylation with allylamine in the presence of Pt catalyst. Temperature of the reaction as well as a strength of the reducing agent (LiAlH_4 , $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$, LiBH_4 , NaBH_4) strongly affect GeQDs yield, particle size and corresponding photoluminescence.⁵

Contrary to germanium halides, solution synthesis Ge nanoparticles (GeNPs) via reduction of germanium (IV) alkoxides has not been described in the literature.⁵ Recently, Ozin et

al. reported a new method of preparation of ultra-small amorphous GeNPs by hydrolysis and condensation reaction between trialkoxysilane and Ge(IV)-alkoxides.⁶ The produced reddish-brown gel consisting of amorphous GeNPs embedded in silica matrix. The silica gel obtained must be dried and ground in to the powder containing amorphous GeNPs. Subsequently, the amorphous GeNPs can be converted to crystalline GeNPs by annealing at 600 °C in the oxygen free environment. The dangerous HF etching process is required to liberate c-GeNPs from the silica matrix.

Most of the reported methods for the preparation of Ge nanoparticles include reactions at high temperature, in the presence of strong reducing agents and harmful compounds such as HF, which puts in question large scale synthesis of the Ge nanoparticles. There is a continuous search for new, economical and easy to scale up methods for the preparation of germanium nanoparticles.

Object of the Invention

It is an object of the present invention to provide a method for preparing germanium nanoparticles from non-hazardous reagents in a simple one-pot process performed at a relatively low temperature.

Summary of the Invention

This object is resolved by a process for preparing blue luminescent germanium nanoparticles comprising the following steps:

- (a) reacting a mixture containing
 - (1) at least one germanium(IV)-alkoxide;

(2) at least one organosilane and/or organosiloxane containing at least one Si-H group per molecule in at least one hydrocarbon solvent; and
(3) a catalytic amount of Lewis acid catalyst according to formula (V)



wherein

each R^5 is independently selected from substituted or unsubstituted aromatic radicals having from 5 to 14 carbon atoms;

X is a halogen atom;

x is 1, 2, or 3; and

y is 0, 1 or 2;

with the proviso that $x + y = 3$, and the further proviso that the catalyst comprises at least one electron withdrawing group;

under stirring under inert atmosphere at a temperature in the range of from 80 °C to 300 °C, wherein the molar ratio of germanium(IV)-alkoxide to Si-H groups is in a range of from 1:4 to 1:10; and

(b) stabilizing germanium nanoparticles by adding at least one surface bonding agent or by exposure to the ambient air.

Detailed Description of the Invention

The present invention shows that the reaction of Ge(IV)-alkoxides with organosilanes and/or organosiloxanes containing at least one Si-H group in the molecule in the presence of catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ at moderately elevated temperature of about 80 °C or higher under inert atmosphere leads to the reduction of the Ge(IV)-alkoxide to Ge(0) and subsequently to the formation of germanium containing nanoparticles.

Typically, nanoparticles are particles between 1 and 100 nanometers (nm) in size. According to the present invention the size of germanium nanoparticles is in a range of from 1 nm to about 100 nm.

5

According to the present invention any available germanium(IV)-alkoxide can be applied.

Germanium(IV)-alkoxides are preferably those of general formula (I)

10



wherein

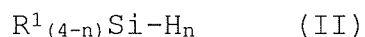
the symbols R, which are identical or different, represent a linear or branched, acyclic or cyclic, saturated or
15 unsaturated, aliphatic C₁-C₂₀ hydrocarbon radical.

Examples for R are methyl, ethyl, vinyl, n-propyl, iso-propyl, allyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, n-
20 hexyl, iso-hexyl, cyclohexyl, n-heptyl, n-octyl, i-octyl.
Preferred examples for R are methyl, ethyl, n-propyl and n-butyl.

According to the present invention, any available organosilane
25 and/or organosiloxane containing at least one Si-H group per molecule can be applied.

Organosilanes containing at least one Si-H group per molecule are preferably those of general formula (II)

30



wherein

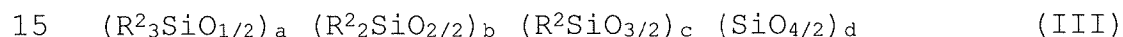
n represents the integer 1 or 2 or 3, and the symbols R^1 , which are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic C_1 - C_{20} hydrocarbon radical.

5

Examples for R^1 are methyl, ethyl, vinyl, n-propyl, iso-propyl, allyl, n-butyl, iso-butyl, n-pentyl, iso-pentyl, n-hexyl, iso-hexyl, cyclohexyl, n-heptyl, n-octyl, iso-octyl, phenyl and tolyl. Preferred examples for R^1 are methyl, ethyl, n-propyl, n-butyl and phenyl.

10

Organosiloxanes containing at least one Si-H group per molecule are preferably those of general formula (III)



wherein

the symbols R^2 , which are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic C_1 - C_{20} hydrocarbon radical, H, or halogen;

20

a represents an integer in the range of from 2 to 60,

b represents an integer in the range of from 0 to 4000,

c represents an integer in the range of from 0 to 50,

25

d represents an integer in the range of from 0 to 30,

with the proviso that at least one symbol R^2 represents H.

Examples for R^2 are H, methyl, ethyl, vinyl, n-propyl, iso-propyl, allyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, n-hexyl, iso-hexyl, cyclohexyl, n-heptyl, n-octyl, iso-octyl, phenyl and tolyl. Preferred examples for R^2 are H, methyl, ethyl, vinyl, n-propyl, n-butyl, iso-octyl and phenyl.

30

In a special embodiment of the present invention the mixture of step a) is obtained by executing the following steps:

(a1) preparing a solution of at least one germanium(IV)-alkoxide in at least one hydrocarbon solvent,

5 (a2) preparing a mixture of at least one organosilane containing at least one Si-H group per molecule and a catalytic amount of Lewis acid catalyst in at least one hydrocarbon solvent,

10 (a3) heating the solution of step (a1) under inert atmosphere to a temperature in the range of from 80 °C to 300 °C,

(a4) combining the solution of step (a2) with the mixture of step (a3) under inert atmosphere and allowing to react under stirring.

15 In another special embodiment of the present invention the mixture of step a) is obtained by executing the following steps:

(a1) preparing a mixture of at least one germanium(IV)-alkoxide and a catalytic amount of Lewis acid catalyst in at least
20 one hydrocarbon solvent,

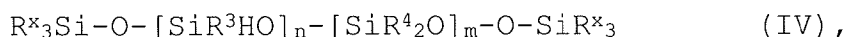
(a2) preparing a solution of at least one organosilane and/or organosiloxane containing at least one Si-H group in at least one hydrocarbon solvent,

25 (a3) heating the solution of step (a1) under inert atmosphere to a temperature ≥ 80 °C,

(a4) combining the solution of step (a2) to the mixture of step (a3) under inert atmosphere and allowing to react under stirring.

30 Preferably, the organosilanes and/or organosiloxanes are selected from the group consisting of PhMe_2SiH , Ph_2SiH_2 , PhMeSiH_2 , PhSiH_3 , $\text{H}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{H}$, poly(methylhydrosiloxanes) $\text{Me}_3\text{Si-O}[\text{Si}(\text{Me})\text{H-O}]_n\text{-SiMe}_3$, wherein n is an integer in the

range of from 1 to 4000, and polysiloxane copolymers of the general formula (IV)



5

wherein the symbols R^* are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic $\text{C}_1\text{-C}_{20}$ hydrocarbon radical, H or halogen;

10 the symbols R^3 and R^4 are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic $\text{C}_1\text{-C}_{20}$ hydrocarbon radical; m represents an integer in the range of from 1 to 1000, and n represents an integer in the range of from 1 to 1000.

15 Examples for R^* , R^3 and R^4 are the same groups as mentioned above for R^2 .

It is advantageous to the process of the present invention to be conducted under inert atmosphere. The process can be

20 conducted under atmospheric pressure, but it could also be conducted under higher pressure, too. However, it is preferred to conduct the present invention under atmospheric pressure.

The temperature is an essential feature and must be in a range of from 80 °C to 300 °C, preferably the temperature is in a range of from 90 °C to 240 °C, more preferably the temperature is in a range of from 100 °C to 200 °C.

25

According to the present invention a hydrocarbon solvent is employed. Preferably, the hydrocarbon solvent is selected from acyclic saturated hydrocarbons and aromatic hydrocarbons. Preferred solvents are toluene, xylene, mesitylene and heptane.

30

It is advantageous to the process of the present invention to be conducted in an anhydrous hydrocarbon solvent.

The nanoparticles can be stabilized by a surface bonding agent or by exposure to ambient air. The surface bonding agent is not critical. The skilled artisan can apply any known surface bonding agent. However, alpha olefins with aliphatic chain or aliphatic amines or imidazoles or organic thiols are preferred. Wherein the group consisting of octene, decene, undecene, allylamine, oleylamine and decylamine is most preferred.

As noted, the method of the present invention requires the use of an appropriate catalyst. The catalyst is a Lewis acid catalyst of formula (V),



wherein

each R^5 is independently selected from substituted or unsubstituted aromatic radicals having from 5 to 14 carbon atoms;

X is a halogen atom;

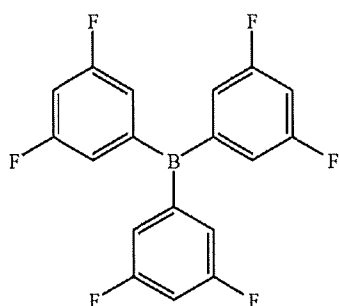
x is 1, 2, or 3; and

y is 0, 1 or 2;

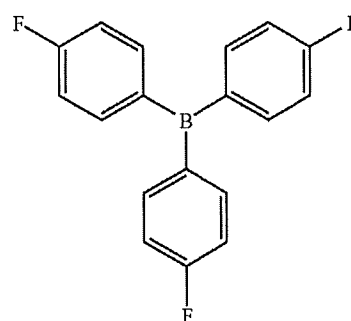
with the proviso that $x + y = 3$, and the further proviso that the catalyst comprises at least one electron withdrawing group.

Suitable electron withdrawing groups include halogen atoms, $-\text{CF}_3$ groups, $-\text{NO}_2$ groups, and $-\text{CN}$ groups. The at least one electron withdrawing group may be a functional group forming a part of R^5 , or the electron withdrawing group may be directly bound to the boron group, as is the case when y is 1 or 2 (see for example formulae XII, XIII, XVI, and XVII).

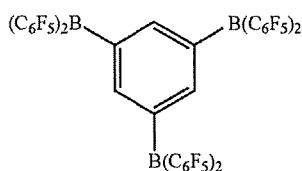
In one embodiment, the catalyst comprises at least one group R^5 which is an aromatic radical having from 5 to 14 carbon atoms, said group R^5 being substituted with at least two halogen atoms. In one embodiment, each R^5 is unsubstituted phenyl and X is
 5 halogen (see for example, formulae XVI and XVII below). Typical examples of such organic Lewis acid catalysts represented by formula (V) include, but are not limited to:



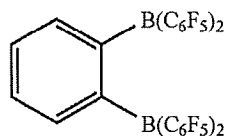
(VI)



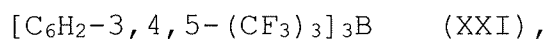
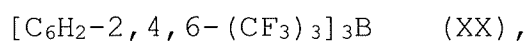
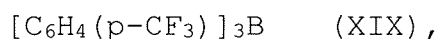
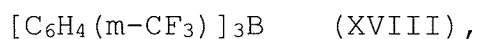
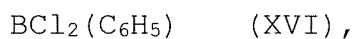
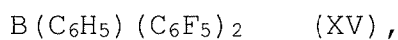
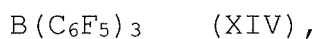
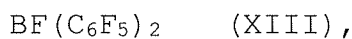
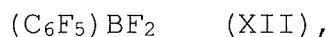
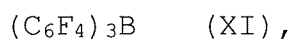
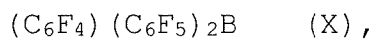
(VII)



(VIII)



(IX)



where in structures (X) and (XI), the four fluorine atoms can

be substituted either on the 2,3,4,5,6 positions and the remaining carbon valence is substituted by hydrogen.

$B(C_6F_5)_3$ is the most preferred catalyst.

- 5 The catalyst is applied in a catalytic amount. Preferably, the catalyst is added in a concentration range of from 0.01 to 10 mol-% with regard to the molar amount of Si-H groups.

10 **Examples**

Materials

Phenyldimethylsilane (Fluorochem, 98 %), triethylsilane (Aldrich, 99 %), germanium n-butoxide (ABCR, 95 %),
15 tris(pentafluorophenyl)borane (TCI, >97 %) were used without further purification. Poly(methylhydrosiloxane) (ABCR, viscosity 15-25 cSt) was dried under $MgSO_4$. Solvents: toluene, methylene chloride, heptane were dried by refluxing and subsequent distillation over CaH_2 . The distilled solvents were
20 stored in a dry box system.

NMR spectroscopy

1H , ^{13}C , ^{29}Si -NMR spectra in $CDCl_3$ were obtained with a Bruker 500 MHz spectrometer. ^{29}Si -NMR spectra were recorded with
25 broadband proton decoupling. A heteronuclear gated decoupling with 20 s delay technique was used to acquire ^{29}Si -NMR spectra.

IR spectroscopy

FT-IR spectra were recorded by a Nicolet 380 spectrophotometer.
30 Analyzed sample was placed between two KBr plates or in cuvette with ZnSe windows. FTIR-ATR spectra were recorded using the Nicolet 6700 apparatus equipped with id7 ATR accessory.

Gas chromatography-mass spectrometry (GC/MS)

GC/MS analysis was performed using a Shimadzu QP2010 ultra apparatus equipped with Zebron ZB-5MSi Capillary GC Column
5 (30 m × 0.25 mm × 0.25 μm). Carrier gas was helium. The following temperature program was used: Hold at 50 °C for 3 min, heat to 250 °C at a rate of 10 °C/min, hold at 250 °C for 20 min, heat to 280 °C at a rate 20 °C/min. Quadrupole mass spectrometer, Shimadzu QP2010 Ultra, with electron ionization
10 was connected to a GC system.

UV-Vis spectroscopy

UV-Vis spectra were recorded using a Specord S600 (Zeiss, Jena, Analytik Jena AG, Jena, Germany) UV-VIS spectrometer equipped
15 with 8-cell changer position with temperature control unit. Analysis were completed under dry nitrogen using 0.1 cm quartz cuvette equipped with Teflon stopcock.

Dynamic Light Scattering (DLS) measurements

20 Size and size distribution of nanoparticles were measured using Zeta Sizer 3000 HAS (Malvern Instrument) in dry toluene.

SEM and EDS measurements

Scanning electron microscopy (SEM) observations were performed
25 on a low vacuum Scanning Electron Microscope JSM 5500 by JEOL, equipped with energy-dispersive X-ray spectrometer EDX.

Transmission Electron Microscopy (TEM)

High-resolution (TEM) of nanoparticles were conducted using
30 Talos F200x by FEI, equipped with a scanning system (STEM) and energy-dispersive X-ray spectrometer EDX.

X-ray Fluorescence Spectroscopy (XRF)

Content of the Ge in toluene was determined by XRF. Germanium content measurement was performed using WDXRF spectrometer Panalytical Axios mAX, equipped with Rh SST-mAX, 4 kW lamp.

5 Measurements were made in helium atmosphere. The detection time of germanium has been significantly extended to obtain a small statistical error due to the number of fluorescent photon counts. The measurement results were calculated using the Omnician resident program and calibration of the spectrometer
10 based on a series of synthetic standards.

Photoluminescence

Photoluminescence measurements were performed using Fluorolog-3 22 instrument (Horiba Jobin-Yvon). Photoluminescence lifetimes
15 were obtained using a time-correlated single-photon counting (TCSPS) accessory (Horiba) and fluorescence decay analysis software (DAS6).

Comparative Example 1: Reaction of Ge(OBu)₄ with PhMe₂SiH in the
20 presence of B(C₆F₅)₃ at 25°C (in accordance with procedure 2 in
Organometallics 2018, 37, 1585-1590)⁷

All operations in preparation of the reaction mixture were performed under the atmosphere of dry nitrogen in the glove box. The solution of germanium (IV)-butoxide (Ge(OBu)₄)
25 (1.80 g, 4.93 x 10⁻³ mol, 1 mol/L) dissolved in 3.0 mL of dried toluene was placed in a 50 mL three necked flask purged with nitrogen, equipped with magnetic stirrer, and gaseous products outlet connected via double-tipped needle to an upturned burette filled with silicone oil. Separately, 12 mL of the
30 toluene solution containing (3.09 g, 0.0227 mol, 1.5 mol/L) of phenyldimethylsilane (PhMe₂SiH) and (0.0974 g, 1.902 x 10⁻⁴ mol) of tris(pentafluorophenyl)borane (B(C₆F₅)₃) was transferred to 20 ml Hamilton syringe. This solution was slowly added over a

period of 2 h to the stirred solution of $\text{Ge}(\text{OBu})_4$ by means of a syringe pump through a septum at room temperature about 22 °C. Moderate gas evolution was observed during addition of the silane. The temperature of the reaction mixture was maintained below 30 °C. 113.7 mL of the gas was collected when the addition was completed. Reaction was continued for an additional hour at RT. The total volume of the collected gas was 118 mL, which corresponds to about 95 % of the expected volume of GeH_4 , assuming 95 % conversion of $\text{Ge}(\text{OBu})_4$. A sample of the captured gas was withdrawn by means of hypodermal syringe from the burette, mixed with cold CDCl_3 and subjected to analysis by ^1H NMR and GC/MS. ^1H NMR (CDCl_3) δ : 3.20ppm (s), confirmed presence of GeH_4 . Purity of the collected GeH_4 was estimated at 95 %.

Comparative Example 2: Reaction of $\text{Ge}(\text{OEt})_4$ with PhMe_2SiH in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at 100 °C

All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of germanium(IV)-ethoxide (0.489 g, 1.9×10^{-3} mol) dissolved in 4.9 mL of dried toluene was placed in a 25 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of PhMe_2SiH (1.37 g, 10.1×10^{-3} mol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.016 g, 3.1×10^{-5} mol) were dissolved in 3.6 mL of dried toluene. This solution was introduced to the stirred solution of $\text{Ge}(\text{OEt})_4$ in toluene at 100 °C by means of a syringe through septum over a period of 10 min. The final concentration of $\text{Ge}(\text{OEt})_4$ in reaction mixture was about 0.22 mol/L. Color of the reaction mixture gradually changed from colorless to orange. Formation of solid material was observed after 20 min of heating at 100 °C. The obtained solid was separated from the liquid phase, washed with toluene and dried on high vacuum.

SEM/EDS analysis of the obtained yellow powder confirmed presence of Ge. DSL analysis of the orange solution showed a presence of nanoparticles in the broad range from ~200 nm to ~1000 nm.

5 Analysis: DLS = 200-1000 nm; no emission

Example 1: Reaction of $\text{Ge}(\text{OBu})_4$ with PhMe_2SiH in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ at 100 °C leading to the formation of Ge-NPs in toluene

All operations in preparation of the reaction mixtures were
10 performed under the atmosphere of nitrogen. The solution of $\text{Ge}(\text{OBu})_4$ (0.62 g, 1.7 mmol) in 7.5 ml of dried toluene was placed in a 100 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of PhMe_2SiH
15 (1.13 g, 8.3 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.021 g, 0.041 mmol, 0.5 mol-% based on SiH groups) in 41 ml of dried toluene was transferred to Hamilton syringe. This solution was introduced to the stirred toluene solution of $\text{Ge}(\text{OBu})_4$ at 100 °C by means of a syringe through septum over a period of 10 min. The final
20 concentration of $\text{Ge}(\text{OBu})_4$ in the reaction mixture was about 0.034 mol/L. Reaction mixture was hold at 100 °C. Color of the reaction mixture changed from colorless to dark yellow over a period of 2 h. ^1H -NMR analysis of the reaction mixture showed 70 % conversion of $\text{Ge}(\text{OBu})_4$ and 60 % conversion of PhMe_2SiH . A
25 second portion of 0.5 mol-% of tris(pentafluorophenyl)borane (0.021 g, 0.041 mmol) in 1 ml of dried toluene was introduced to the reaction mixture. Further change of the color from yellow to dark reddish over the next two hours was observed. ^1H -NMR and ^{29}Si -NMR analysis of the final mixture showed the
30 complete consumption of $\text{Ge}(\text{OBu})_4$, formation of $\text{PhMe}_2\text{SiOBu}$ and small fraction of the residual PhMe_2SiH . The reaction mixture was cooled down to room temperature. DLS measurement of the final solution showed presence of nanoparticles with an average

size of 7 nm. The presence of nanoparticles was confirmed by TEM. The color of the transparent, dark red solution faded during exposure to the ambient air and eventually became colorless after 5 days of exposure. Blue photoluminescence of the final colorless solution was observed when irradiated with UV light.

Analysis: HRTEM = 5 - 20 nm; DLS = 7 nm; emission 413 nm (under irradiation with 350 nm)

Example 2: Reaction of $\text{Ge}(\text{OBu})_4$ with PhMe_2SiH in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene. Effect of reaction temperature.

All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of $\text{Ge}(\text{OBu})_4$ (0.62 g, 1.7 mmol) in 7.5 ml of dried toluene was placed in a 100 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of PhMe_2SiH (1.13 g, 8.3 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.021 g, 0.041 mmol, 0.5 mol-% based on SiH groups) in 41 ml of dried toluene was transferred to Hamilton syringe. This solution was introduced to the stirred toluene solution of $\text{Ge}(\text{OBu})_4$ at desired temperature by means of a syringe through septum over a period of 10 min:

Experiment 2a, Temp = 20 °C;

Experiment 2b, Temp = 40 °C;

Experiment 2c, Temp = 60 °C;

Experiment 2d, Temp = 80 °C;

Experiment 2e, Temp = 100 °C.

The final concentration of $\text{Ge}(\text{OBu})_4$ in reaction mixture was about 0.034 mol/L. The reaction mixture was hold at the desired temperature over 2 h. A second portion of 0.5 mol-% of $\text{B}(\text{C}_6\text{F}_5)_3$ was introduced to the reaction mixture. The complete conversion of $\text{Ge}(\text{OBu})_4$ was confirmed in each case by ^1H -NMR. The reaction mixture was hold at the desired temperature for additional

12 h. Finally, the reaction mixture was cooled down to room temperature. Content of germanium in the final transparent solutions was determined by XRF, Table 1.

Analysis: Example 2e, DLS = 10 - 50 nm

5

Example 3: Reaction of $\text{Ge}(\text{OBu})_4$ with PhMe_2SiH in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ in mesitylene. Effect of reaction temperature.

All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of
10 $\text{Ge}(\text{OBu})_4$ (0.295 g, 0.807 mmol) in 3.6 ml of dried mesitylene was placed in a 50 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of PhMe_2SiH (0.52 g, 3.83 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.01 g, 0.019 mmol) in 19 ml
15 of dried toluene was transferred to Hamilton syringe. This solution was introduced to the stirred mesitylene solution of $\text{Ge}(\text{OBu})_4$ at desired temperature by means of a syringe through septum over a period of 10 min:

Experiment 3a, Temp = 130 °C;

20 Experiment 3b, Temp = 160 °C.

The final concentration of $\text{Ge}(\text{OBu})_4$ in reaction mixture was about 0.035 mol/L. The reaction mixture was hold at the desired temperature over 2 h. Next, the second portion of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.01 g, 0.019 mmol) in 1 ml of dried mesitylene was introduced
25 the reaction mixture. The complete conversion of $\text{Ge}(\text{OBu})_4$ was confirmed in each case by ^1H -NMR. The reaction mixture was hold at the desired temperature for additional 12 h. Finally, the reaction mixture was cooled down to room temperature. Content of germanium in the final dark red transparent solutions was
30 determined by XRF, Table 1.

Analysis: Example 3a DLS = 7-80 nm

Table 1. Amount of germanium present in the final solutions obtained in Examples 2a, 2b, 2c, 2d, 2e, 3a and 3b determined by XRF

Example	Reaction Temp. / °C	Color of the final solution	[Ge] / wt-%	% Yield of Ge nanoparticles
2a	20	Colorless	0.037	14
2b	40	Colorless	0.044	20
2c	60	Straw	0.04	15
2d	80	Orange	0.115	46
2e	100	Dark red	0.218	85
3a	130	Dark red	0.212	80
3b	160	Dark red	0.253	95

5 These examples show the effect of the reaction temperature on the yield of Ge. A significant amount of Ge nanoparticles suspended in the solvent is produced at a temperature of 80 °C or above as it is indicated by the formation of dark red transparent solutions and confirmed by XRF analysis.

10 Example 4: Reaction of Ge(OBu)₄ with PhMe₂SiH in the presence of B(C₆F₅)₃ in toluene at 100°C. Effect of Ge(OBu)₄ concentration in the final reaction mixture.

15 All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of 1 mole equivalent of Ge(OBu)₄ at desired concentration (see Table 2) in dried toluene was placed in a 100 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the
20 desired solution of about 5 mole equivalents of PhMe₂SiH containing 0.5 mol-% of B(C₆F₅)₃ – based on SiH groups – in dried toluene (see Table 2) was transferred to Hamilton syringe. This solution was introduced to the stirred toluene solution of Ge(OBu)₄ at 100 °C through septum over a period of

10 to 20 min. The reaction mixture was hold at 100 °C for 2 h. A second portion of 0.5 mol-% of B(C₆F₅)₃ in dried toluene was introduced to the reaction mixture. The reaction mixture was hold at the desired temperature for additional 12 h. The
 5 complete conversion of Ge(OBu)₄ was confirmed in each case by ¹H-NMR. Finally, the reaction mixture was cooled down to room temperature. The final samples were examined for a presence of visible precipitate, Table 2. The formed solid (Example 4a and 4b) were isolated, washed with fresh toluene and analyzed by
 10 SEM/EDS. SEM/EDS confirmed the presence of Ge.

The presented results of Example 4 show that the transparent dispersion of Ge nanoparticles in toluene at 100 °C can be prepared from the solution of Ge(IV)-butoxide when the
 15 concentration of Ge(OBu)₄ in the final reaction mixture is below 0.070 mol/L. Most preferably below 0.035 mol/L. From the practical point of view the minimum concentration of Ge nanoparticles prepared by this process could be set at about 0.0001 mol/L.

20

Table 2. Reaction of Ge(OBu)₄ with PhMe₂SiH in the presence of B(C₆F₅)₃ in toluene at 100 °C. Effect of initial reagents concentration and the final concentration of Ge(OBu)₄ in reaction mixture on the formation of solid precipitate.

25

Example	[Ge(OBu) ₄]o mol/L	[PhMe ₂ SiH]o mol/L	Final [Ge(OBu) ₄] mol/L	Solid Formation
4a	0.8	0.8	0.14	Yes
4b	0.4	0.4	0.070	Yes
4c	0.2	0.2	0.034	No
4d	0.1	0.1	0.017	No

Example 5: Reaction of $\text{Ge}(\text{OBu})_4$ with PhMeSiH_2 in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ in heptane at 80 °C

All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of $\text{Ge}(\text{OBu})_4$ (1.75 g, 4.8×10^{-3} mol) dissolved in 13.0 mL of dried heptane was placed in a 50 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of PhMeSiH_2 (1.53 g, 1.25×10^{-2} mol, 0.16 mol/L) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.02 g, 3.9×10^{-5} mol) were dissolved in 6.5 mL of dried heptane. This solution was introduced to the stirred solution of $\text{Ge}(\text{OBu})_4$ in heptane at 80 °C by means of a syringe through septum over a period of about 10 min. Gas evolution was observed during the silane addition. Color of the reaction mixture gradually changed from colorless to yellow. Reaction mixture was hold at 80 °C for an additional 12 h and finally cooled down to RT. Formation of solid material was not observed. The color of the final solution slowly faded when exposed to an ambient air for several hours. This solution does not show any PL under UV light irradiation. The subsequent treatment of this solution with 1-decene at 80 °C leads to the formation of colorless solution, which shows blue photoluminescence under UV light. TEM analysis of the final solution applied on the TEM grid and treated for 2 h at 500 °C showed presence of 10 - 30 nm particles.

Analysis: HRTEM = 10 - 30 nm; DLS = 12 nm; emission 410 nm (under irradiation with 350 nm)

Example 6: Reaction of diluted $\text{Ge}(\text{OBu})_4$ with PHMS in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at 100 °C

All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of $\text{Ge}(\text{OBu})_4$ (0.10 g, 2.8×10^{-4} mol, 0.1 mol/L) and $\text{B}(\text{C}_6\text{F}_5)_3$

(0.021 g, 4.1×10^{-5} mol) dissolved in 2.9 mL of dried toluene was placed in a 25 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately, a low viscosity poly(methylhydrosiloxane) ($n = 26$, $M_n \sim 1600$) containing 0.016 mol/g of Si-H groups (0.081 g, 1.26×10^{-3} mol of SiH, 0.1 mol/L) was dissolved in 12.2 mL of dried toluene. This solution was introduced to the stirred solution of $\text{Ge}(\text{OBu})_4$ with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at 100 °C by means of a syringe through septum over a period of 10 min. The final concentration of $\text{Ge}(\text{OBu})_4$ in reaction mixture was about 0.018 mol/L. Color of the reaction mixture gradually changed from colorless to orange. Formation of solid material was not observed after 20 min of heating at 100 °C. The final transparent, dark orange solution did not show any photoluminescence under UV light irradiation. 1 ml of the final solution was mixed with 100 ml of oleylamine. The produced mixture became colorless after 16 h of mixing at RT and showed blue photoluminescence under UV light (410 nm when irradiated with 350 nm light). SEM/EDS analysis of the solids obtained by removal of volatiles from the final solution confirmed presence of Ge embedded in siloxane matrix.

Analysis: emission 410 nm (under irradiation with 350 nm)

Example 7: Preparation of blue fluorescent Ge nanoparticles by reaction of $\text{Ge}(\text{OBu})_4$ with PhMe_2SiH in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene and post-treatment with amines

All operations in preparation of the reaction mixtures were performed under the atmosphere of nitrogen. The solution of $\text{Ge}(\text{OBu})_4$ (0.605 g, 1.66 mmol) in 7.5 ml of dried toluene was placed in a 100 mL flask purged with nitrogen, equipped with magnetic stirrer, nitrogen gas inlet and gaseous products outlet through a bubbler. Separately the solution of PhMe_2SiH

(1.11 g, 8.2 mmol) and $B(C_6F_5)_3$ (0.02 g, 0.039 mmol, 0.5 mol-% based on $PhMe_2SiH$) in 41.7 ml of dried toluene was transferred to Hamilton syringe. This solution was introduced to the stirred toluene solution of $Ge(OBu)_4$ at 100 °C by means of a syringe through septum over a period of 10 min. The final concentration of $Ge(OBu)_4$ in reaction mixture was about 0.033 mol/L. Reaction mixture was hold at 100 °C. The second portion of 0.5 mol-% of $B(C_6F_5)_3$ (0.021 g, 0.041 mmol) in 1 ml of dried toluene was introduced the reaction mixture after 2 h of mixing at 100 °C. The reaction was hold at 100 °C for an additional 1 h and next was cooled down to room temperature. XRF analysis confirmed a presence of 80 % of the starting Ge in the final product. 1 ml samples of the final solution were mixed with 100 μ l of selected amines or decene and heated at 100 °C for 1 h and left overnight at RT. The color of the formed dispersions changed to colorless and the resulting mixture showed photoluminescence when irradiated with UV light (see Table 3).

Table 3. Reaction of $Ge(OBu)_4$ with $PhMe_2SiH$ in the presence of $B(C_6F_5)_3$ in toluene and post-treatment with amines and decene.

Example	Surface bonding agent	Emission(excitation = 350 nm)
7a	Decylamine	404 nm
7b	Oleylamine	417 nm
7c	Allylamine	432 nm
7d	Decene	410 nm

The above presented results show that the reaction of Ge(IV) alkoxides with Si-H functional organosilanes and/or organosiloxanes in the presence of catalytic amounts of $B(C_6F_5)_3$ at moderately elevated temperature from about of 80 °C or

higher under inert atmosphere and atmospheric or higher pressure reduces Ge(IV)-alkoxide to Ge(0) and form germanium containing nanoparticles. The most preferred temperature is 100 °C or higher. The formed nanoparticles may stay suspended in the organic solvent or form aggregates which fall out of the solution. The concentration of Ge alkoxide in the final solution controls the fraction of the formed Ge(0) nanoparticles suspended in the organic solvent. The preferred final concentration of germanium alkoxide in the organic solvent, after addition of the silane was completed, is in the range from about 0.070 to 0.0001 mol/L.

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Claims

1. A process for preparing blue luminescent germanium nanoparticles comprising the following steps:

- 5 (a) reacting a mixture containing
- (1) at least one germanium(IV)-alkoxide;
 - (2) at least one organosilane and/or organosiloxane containing at least one Si-H group per molecule in at least one hydrocarbon solvent; and
 - 10 (3) a catalytic amount of Lewis acid catalyst according to formula (V)



- 15 wherein
- each R^5 is independently selected from substituted or unsubstituted aromatic radicals having from 5 to 14 carbon atoms;
- X is a halogen atom;
- 20 x is 1, 2, or 3; and
- y is 0, 1 or 2;
- with the proviso that $x + y = 3$, and the further proviso that the catalyst comprises at least one electron withdrawing group;
- 25 under stirring under inert atmosphere at a temperature in the range of from 80 °C to 300 °C, wherein the molar ratio of germanium(IV)-alkoxide to Si-H groups is in a range of from 1:4 to 1:10; and
- (b) stabilizing germanium nanoparticles by adding at
- 30 least one surface bonding agent or by exposure to the ambient air.

2. The process according to claim 1, wherein the mixture of step a) is obtained by executing the following steps:

(a1) preparing a solution of at least one germanium(IV)-alkoxide in at least one hydrocarbon solvent,

(a2) preparing a mixture of at least one organosilane containing at least one Si-H group per molecule and a catalytic amount of Lewis acid catalyst in at least one hydrocarbon solvent,

(a3) heating the solution of step (a1) under inert atmosphere to a temperature in the range of from 80 °C to 300 °C,

(a4) combining the solution of step (a2) with the mixture of step (a3) under inert atmosphere and allowing to react under stirring.

3. The process according to claim 1, wherein the mixture of step a) is obtained by executing the following steps:

(a1) preparing a mixture of at least one germanium(IV)-alkoxide and a catalytic amount of Lewis acid catalyst in at least one hydrocarbon solvent,

(a2) preparing a solution of at least one organosilane and/or organosiloxane containing at least one Si-H group in at least one hydrocarbon solvent,

(a3) heating the solution of step (a1) under inert atmosphere to a temperature ≥ 80 °C,

(a4) combining the solution of step (a2) to the mixture of step (a3) under inert atmosphere and allowing to react under stirring.

4. The process according to anyone of claims 1-3, wherein the germanium(IV)-alkoxide is a germanium(IV)-alkoxide according to formula (I)

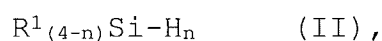


wherein

the symbols R, which are identical or different, represent a linear or branched, cyclic or acyclic, saturated or unsaturated, aliphatic C₁-C₂₀ hydrocarbon radical.

5

5. The process according to anyone of claims 1-4, wherein organosilanes according to general formula (II)



10

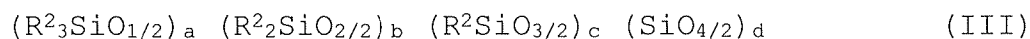
wherein

n represents the integer 1 or 2 or 3 and

the symbols R¹, which are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic C₁-C₂₀ hydrocarbon radical; and

15

organosiloxanes according to general formula (III)



20

wherein

the symbols R², which are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic C₁-C₂₀ hydrocarbon radical, H, or halogen;

25

a represents an integer in the range of from 2 to 60,

b represents an integer in the range of from 0 to 4000,

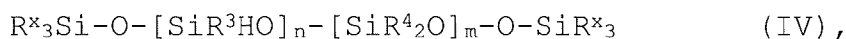
c represents an integer in the range of from 0 to 50,

d represents an integer in the range of from 0 to 30,

30

with the proviso that at least one symbol R² represents H; are applied.

6. The process according to anyone of claims 1-5, wherein the organosilane and/or organosiloxane is selected from the group consisting of PhMe_2SiH , Ph_2SiH_2 , PhMeSiH_2 , PhSiH_3 , $\text{H}(\text{Me})_2\text{SiOSi}(\text{Me})_2\text{H}$, poly(methylhydrosiloxanes) $\text{Me}_3\text{Si-O-}$
5 $[\text{Si}(\text{Me})\text{H-O}]_n\text{-SiMe}_3$, wherein n is an integer in the range of from 1 to 4000, and polysiloxane copolymers of the general formula (IV)



10 wherein the symbols R^* are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic $\text{C}_1\text{-C}_{20}$ hydrocarbon radical, H or halogen;

15 the symbols R^3 and R^4 are identical or different, represent a linear or branched, acyclic or cyclic, saturated or unsaturated, aliphatic or aromatic $\text{C}_1\text{-C}_{20}$ hydrocarbon radical;

20 m represents an integer in the range of from 1 to 1000, and

n represents an integer in the range of from 1 to 1000.

7. The process according to anyone of claims 1-6, wherein the temperature is a range of from 80 °C to 300 °C.

8. The process according to claim 7, wherein the temperature is in a range of from 90 °C to 240 °C.

9. The process according to claim 8, wherein the temperature is in a range of from 100 °C to 200 °C.

10. The process according to anyone of claims 1-9, wherein the catalyst is tris(pentafluorophenyl)borane.

11. The process according to anyone of claims 1-10, wherein the catalyst is added in two equal portions.
- 5 12. The process according to anyone of claims 1-11, wherein the solvent is selected from the group consisting of acyclic saturated, cyclic saturated and aromatic hydrocarbons.
- 10 13. The process according to anyone of claims 1-12, wherein the catalyst is added in a concentration range of from 0.01 to 10 mol-% with regard to the molar amount of Si-H groups.
- 15 14. The process according to anyone of claims 1-13, wherein the process is executed under atmospheric pressure.
15. The process according to anyone of claims 1-14, wherein the surface bonding agent is selected from alpha olefins with aliphatic chain or aliphatic amines or imidazoles or
20 organic thiols.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/052672A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/66 B22F9/24
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)
C09K C22C B22F

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.
A	ÖMER DAG ET AL: "Synthesis of Nanoamorphous Germanium and Its Transformation to Nanocrystalline Germanium", SMALL, vol. 8, no. 6, 9 January 2012 (2012-01-09) , pages 921-929, XP055626862, DE ISSN: 1613-6810, DOI: 10.1002/sml.201101993 cited in the application the whole document ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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Date of the actual completion of the international search

27 September 2019

Date of mailing of the international search report

09/10/2019

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Vanier, Cécile

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/052672

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CAROLAN DARRAGH: "Recent advances in germanium nanocrystals: Synthesis, optical properties and applications", PROGRESS IN MATERIALS SCIENCE, vol. 90, 22 July 2017 (2017-07-22), pages 128-158, XP085199435, ISSN: 0079-6425, DOI: 10.1016/J.PMATSCI.2017.07.005 cited in the application pages 130-136 -----	1-15
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