

BORATE OF LANTHANUM, LUTETIUM, YTTRIUM OR GADOLINIUM
COMPRISING TWO DOPING AGENTS AND ITS PRECURSOR AND USE IN
PLASMA OR X-RAY SYSTEMS

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The present invention relates to a borate of lanthanum, lutetium, yttrium or gadolinium comprising two doping agents, its precursor and its use in plasma or X-ray systems.

10 Plasma systems (screens and lamps) are some of the new techniques for visualization and illumination being developed. A specific example is the replacement of current television screens by flat screens which are lighter and smaller; plasma screens are the current replacement solution.

In plasma systems, a gas introduced into a chamber is ionized under the effect of an
15 electrical discharge. High-energy electromagnetic radiation is emitted during this process. The photons are directed towards a luminescent material.

Furthermore, in systems which use X-rays, the photons excite a luminescent material.

To be effective, that material must be a luminophore that absorbs in the emission range of the plasma or X-rays, emitting in the visible range with a good yield.

20 Rare earth borates are known to be suitable materials of this type. However, products must be found with a further improved luminous yield.

The aim of the invention, therefore, is to obtain materials with an improved luminous yield.

To this end, the rare earth borate of the invention corresponds to the formula LnBO_3 ,
25 and it is characterized in that Ln represents one or more rare earths selected from lanthanum, lutetium, yttrium and gadolinium, and in that it also comprises at least one first element selected from trivalent elements that are capable of capturing electrons and at least one second element selected from trivalent elements that are capable of capturing holes, and europium II.

30 The invention also relates to a process for preparing such a rare earth metal borate which is characterized in that a carbonate or hydroxycarbonate of a rare earth and said elements are reacted with boric acid, the reaction medium being in the form of an aqueous solution, and the reaction product is calcined.

Other characteristics, details and advantages of the invention will become more apparent from the following description and specific non-limiting examples intended to illustrate it.

5 The borate of the invention is based on one or more Ln rare earths that can form the matrix of the product with boron. Ln represents at least one rare earth selected from lanthanum, lutetium, yttrium and gadolinium, or a combination of at least two of these rare earths. In the case of a combination, any respective proportions of the various rare earths can be used. According to a particular embodiment of the invention, yttrium and gadolinium are present in combination.

10 The borate of the invention also comprises a first and a second additional element, it being possible for these elements to play the role of doping agents.

As stated above, the first element is selected from trivalent elements that are capable of capturing electrons. It is an element for which the effective cross section for capturing electrons is greater than the effective cross section for capturing holes.

15 More particular examples of the first element that can be cited are europium, samarium, thulium and ytterbium, these elements possibly being present by themselves or in combination.

The europium and/or samarium content is preferably in the range 2% to 25%, and more particularly in the range 4% to 15%. This content is expressed in moles of europium and/or samarium with respect to the moles of all the rare earths and the additional elements or
20 the said doping agents of the borate, that is to say the ratio $[D_1]/[\Sigma(Ln+D_1+D_2)]$, D_1 designating the first element or the total of the first elements (in the present case europium and/or samarium) and D_2 designating the second element or the total of the other second elements. The europium used as the doping agent here is europium III.

25 The thulium content is in the range 0.1% to 5%, and that of ytterbium is in the range 1% to 2.5%. The thulium and ytterbium contents are expressed in the same manner as that given above for europium and samarium.

The borate of the invention comprises, in combination with the first element or doping agent, at least one second element selected from europium II and trivalent elements that are
30 capable of capturing holes. These are elements for which the effective cross section for capturing holes is greater than the effective cross section for capturing electrons.

This second element can in particular be selected from cerium, terbium, praseodymium, bismuth, lead, antimony, chromium and iron, it being possible for these

elements to be present by themselves or in combination.

In a particular embodiment of the invention, the first said element can be europium, and the second can be terbium. More particularly, yttrium borate and gadolinium borate in combination can be mentioned which further comprise europium and terbium. In another
 5 particular embodiment, lanthanum borate can be cited which comprises thulium as the first element and terbium as the second element. In a third particular embodiment of the invention, the first element is thulium and the second element is cerium; in this case, the borate can be a gadolinium borate.

The total content of the second element can preferably be between 5 ppm and 1,000
 10 ppm in moles of the second element, this content also being expressed in moles with respect to the moles of all the rare earths and the said elements of the borate, that is to say by the ratio $[D_2]/[(\Sigma(Ln+D_1+D_2))]$. This content can more particularly be between 10 ppm and 500 ppm, and still more particularly be between 30 ppm and 100 ppm.

With the third embodiment, i.e., the borate comprising thulium and cerium, the cerium
 15 content is preferably in the range 0.1% to 15%, in particular in the range 0.5% to 10%, and more particularly in the range 5% to 10%. The thulium content can in particular be in the range 5 ppm to 5000 ppm, more particularly in the range 50 to 5000 ppm.

The borate can be in the form of particles the sizes of which can vary within large proportions. However, the median volume diameter of the particles is generally at most 10
 20 μm , more particularly at most 5 μm , and still more particular it can be between 0.5 and 5 μm .

Throughout the description, the values of the median diameter and dispersion index, an index which will be mentioned later, are the values obtained employing the laser diffraction technique using a granulometer of the Coulter LS 230 type.

According to a particular embodiment of the invention, the borate of the invention can
 25 have a specific morphology, that is to say it can be in the form of cubic, parallelepipedal (platelet) or spherical particles. The shape of the particles depends on the nature of the rare earth which makes up the borate. In the case of lanthanum and lutetium, the borate is in the parallelepipedal form or in plate form, it is in the spherical form in the case of yttrium, and in the cubic form for the combination of the rare earths yttrium and gadolinium. Furthermore,
 30 the borate can have a dispersion index of not more than 0.8. More particularly, this index can be not more than 0.7, and still more particularly not more than 0.6. In the context of the present invention, it is possible to obtain products having a dispersion index of 0.4 or 0.5.

The dispersion index is understood as meaning the ratio:

$$\sigma/m = (d_{90}-d_{10})/2d_{50}$$

in which:

- d_{90} is the equivalent diameter for which the material passing through is equal to 90%;
- d_{10} is the equivalent diameter for which the material passing through is equal to 10%;
- d_{50} is the median diameter of the particles.

The borates of the invention can be obtained by any known process. Processes employing a solid/solid reaction by mixing and melting the precursors of the elements included in the borate composition, for example oxides or carbonates, can be mentioned.

A more particular process will be described below. This process is more particularly applied to preparing a borate which has the morphologies described above (parallelepiped or plate, sphere, cube) and a dispersion index of not more than 0.8.

The process uses, as precursors of the rare earth or earths or doping element or elements included in the borate composition, a carbonate or a hydroxycarbonate of these rare earths or doping agents.

It is possible to start from a mixture of carbonates or hydroxycarbonates of rare earths and various doping agents or of mixed carbonates or hydroxycarbonates of rare earths and doping agents.

The carbonates or hydroxycarbonates of the rare earths are products which are known per se and can be obtained, for example, by precipitating one or more rare earth salts with ammonium carbonate or bicarbonate. These carbonates or hydroxycarbonates can be used directly after precipitation or after an optional washing and/or drying step.

The starting carbonate or hydroxycarbonate is reacted with boric acid. The reaction is preferably conducted under the influence of heat, for example at a temperature in the range 40°C to 90°C.

According to another characteristic of this process, the reaction medium is in the form of an aqueous solution. This means that the amount of water present in the reaction medium is such that the weight ratio of water/boric acid + carbonate is at least 300%, more particularly at least 600%. Still more particularly, this ratio can be at least 1000%.

It is possible to work with an excess of boric acid. This excess can be, for example, between 1 mol% and 250 mol% (that is to say $[B]/[\Sigma(Ln+D_1+D_2)] = 1.01$ to 5).

It may be advantageous to carry out the reaction by eliminating the CO_2 formed during

the course thereof. It can, for example, be eliminated by purging the reaction medium with a neutral gas such as nitrogen. This variation allows products with a finer particle size to be obtained.

A precipitate is obtained at the end of the reaction.

5 According to one variation of the invention, the precipitate can be aged in the reaction medium, preferably by keeping the medium at the same temperature as that at which the reaction was carried out. During this ageing, it is also possible to keep the pH of the ageing medium constant. This pH can be fixed at a given value, which can be, for example, the pH of the reaction mixture at the end of the reaction, that is to say when all of the boric acid has
10 been introduced. The pH can be maintained in this way by adding a base, for example by adding an ammoniacal solution. Ageing can last between 1 and 3 hours.

The precipitate is then separated from the reaction medium by any known means, for example by filtration. The precipitate which has been separated out is optionally washed and then dried. One of the advantages of the process described is that it enables a precipitate
15 which can easily be filtered and washed to be obtained. After drying, an additional washing step can also be carried out with a dilute acid, for example nitric acid, to remove possible traces of carbonate which have not completely reacted.

The precipitate is then calcined.

This calcining step produces the borate. It is generally carried out at a temperature in
20 the range 500°C to 1400°C, more particularly in the range 500°C to 1100°C. It is entirely possible to carry out this calcining step in air. Reducing atmospheres (for example hydrogen) or neutral atmospheres (argon) or mixtures thereof can, of course, also be employed for this calcining step.

The calcining step also allows the luminescence properties of the product to develop.
25 If increased luminescence properties are desired, the calcining will be carried out at a proportionally higher temperature.

One variation of the calcining step may be mentioned. This variation comprises mixing the dried precipitate with boric acid in an amount of acid which can be of the order of 5% to 15%, for example. Calcining is then carried out at a temperature which can be in the
30 range 900°C to 1100°C, for example. This variation provides a borate with good luminescence performances at a relatively low calcining temperature.

The invention also relates to a precursor composition of the borate which has just been described. This composition is characterized in that it is based on boron, one or more rare

earths selected from lanthanum, lutetium, yttrium and gadolinium, at least one first element selected from trivalent elements that are capable of capturing electrons and at least one second element selected from trivalent elements that are capable of capturing holes, and in that it is capable of producing, after calcining, a rare earth borate with formula LnBO_3 , Ln representing the said rare earth or earths, said borate also comprising at least one said first element and at least one said second element. The first element can be selected from europium, samarium, thulium and ytterbium and the second element can be selected from cerium, terbium, praseodymium, bismuth, lead, antimony, chromium and iron.

This composition can be prepared by mixing compounds of boron, of rare earths and of the other said elements, these compounds being selected from those which enable the required borate to be obtained after calcining. These compounds of rare earths and of the other elements can be oxides or carbonates, for example.

The composition can also be prepared by a more particular process of the type described above for the borate. This process is characterized in that a carbonate or a hydroxycarbonate of at least one said rare earth, of at least one said first element and at least one said second element is reacted with boric acid, the reaction medium being in the form of an aqueous solution, and the reaction product is optionally washed and/or dried. All that has been stated above for this process up to producing the precipitate, separation and optional washing and/or drying also applies here. The precipitate obtained is based on a hydroxyborocarbonate of one of or the said rare earths, which can be represented by the formula $\text{LnB}(\text{OH})_4\text{CO}_3$, a hydroxyborocarbonate of at least one said first element and a hydroxyborocarbonate of at least one said second element.

This composition based on hydroxyborocarbonates can have the same morphology characteristics (cubic, parallelepipedal (platelet) or spherical particles) and particle size characteristics (particle size and dispersion index of not more than 0.8 in particular) as have been described above with respect to the borate.

Calcining the precursor composition is carried out at a temperature as described above of at least 500°C sufficient to convert this composition into borate, for example.

The invention furthermore relates to the use of the borate described above as a luminophore in any process for visualization and illumination employing plasma excitation. This is understood to mean processes that employ conditions which are those of plasma systems, that is to say using a gas which, after ionization, emits radiation corresponding at least to wavelengths situated between about 100 nm and about 200 nm, more particularly

between 140 nm and 200 nm.

The invention also relates to systems for visualization and illumination of this type, which comprise a borate according to the invention as the luminophore.

Visualization and illumination systems of this type that may be mentioned are plasma
5 screens and lamps.

The borate of the invention can also be used in any system employing X-rays. X-rays are understood as meaning those made up of photons the energy of which is between about 10 and about 100 Kev.

The invention also relates to X-ray visualization systems; imaging systems, in
10 particular for medical imaging, may be mentioned.

The borate is employed in the production of plasma or X-ray systems in accordance with well-known techniques, for example by serigraphy, electrophoresis or sedimentation.

Examples will now be given.

EXAMPLES

15 Products the final composition of which are as follows are prepared, the contents of doping elements being expressed in the manner given above:

Example 1 (comparison): $Y_{0.726}Gd_{0.218}Eu_{0.056}BO_3$

Example 2: Product of the same composition as example 1 but with 70 ppm terbium.

Example 3 (comparison): $Y_{0.79}Gd_{0.15}Eu_{0.06}BO_3$

20 Example 4: Product of the same composition as example 3 but with 50 ppm praseodymium.

Preparation:

A carbonate suspension of all the rare earths (Ln) included in the composition of the products is prepared by addition, in the course of 1 hour under the influence of heat (60°C), of
25 1.31 l of a 1.3 M/l solution of ammonium bicarbonate to 1.50 l of a solution of a mixture of rare earth nitrates, suitably stirred, in a concentration of 0.7 M/l in proportions such that the molar ratio of CO_3/Ln is equal to 1.6.

A 0.8 M/l boric acid solution is then added to the same medium, while still stirring and under the influence of heat, in the course of 30 minutes such that the molar ratio of B/Ln
30 is equal to 1.5. The suspension obtained is then left to age by keeping the temperature at 60°C and the pH at a minimum of 4.6 by addition of a 6 N ammoniacal solution.

After this maturation phase of 3 hours, a white precipitate is obtained, which is separated off by filtration and then washed with demineralized water.

The moist product is then dried at 60°C overnight and subsequently calcined in a muffle furnace (under air) at 1100°C for 2 hours in the presence of 15% of H₃BO₃, in order to obtain the borate of the rare earths.

The particle size was determined for the product of example 2 by the Coulter technique described above. It should also be mentioned that the measurement was carried out on a dispersion of the calcined product in an aqueous 0.1% by weight solution of sodium hexametaphosphate which had already undergone ultrasonic probe treatment (probe with a tip of 12 mm diameter, 450 W) for 3 minutes. The product of example 2 had a median diameter of 2.3 µm and a dispersion index of 0.48.

Properties:

The intensity of the emission peak at 597 nm under X-ray excitation (XR: 30KV) of the borates prepared, in the form of a powder, was measured as a function of the content of the second element (terbium or praseodymium). The results are shown in table 1 below.

Table 1

Example	Content of second element (ppm)	Emission intensity at 597 nm (arbitrary units)
1	0	100
2	70	130
3	0	100
4	50	125

The intensity of the emission peak at 150 nm under plasma excitation of the products of examples 1 and 2 in the form of a powder is measured with a VUV spectrometer. The results are shown in table 2 below.

Table 2

Example	Second element content (ppm)	Emission intensity at 150 nm (arbitrary units)
1	0	4200
2	70	5100

EXAMPLES 5 AND 6

Two products with the compositions given below were prepared as described in the preceding examples:

Example 5 (comparative): $\text{Gd}_{0.98}\text{Ce}_{0.02}\text{BO}_3$

5 Example 6: $\text{Gd}_{0.99}\text{Ce}_{0.005}\text{Tm}_{0.005}\text{BO}_3$

The intensity of the emission peak at 597 nm of the prepared borates in powder form was measured using X ray excitation (XR: 30 kV). The results are shown in table 3 below.

Example	Intensity
5	0.186
6	0.196

It can be seen that the emission intensity of the compound doped with 0.05% of cerium and 0.5% of thulium was superior to that of a compound containing 2% of cerium.



CLAIMS

1. Rare earth borate with formula LnBO_3 , characterized in that Ln represents one or more rare earths selected from lanthanum, lutetium, yttrium and gadolinium, and in that it also comprises at least one first element selected from trivalent elements that are capable of capturing electrons and at least one second element selected from europium II and trivalent elements that are capable of capturing holes.
2. Borate according to claim 1, characterized in that the first element is selected from europium, samarium, thulium and ytterbium and the second element is selected from cerium, terbium, praseodymium, bismuth, lead, antimony, chromium and iron.
3. Borate according to claim 2, characterized in that the first element is thulium and the second element is cerium.
4. Borate according to claim 1 or claim 2, characterized in that the content of the first element europium or samarium is in the range 2 mol% to 25 mol% of europium or samarium with respect to the moles of all the rare earths and said elements of the borate.
5. Borate according to claim 2, characterized in that the thulium content is in the range 0.1 mol% to 5 mol% of thulium with respect to the moles of all the rare earths and the said elements of the borate.
6. Borate according to claim 2, characterized in that the ytterbium content is in the range 1 mol% to 2.5 mol% of ytterbium with respect to the moles of all the rare earths and said elements of the borate.
7. Borate according to any one of claims 1, 2 and 4 to 6, characterized in that the content of the said second element is in the range 5 ppm to 1000 ppm in moles of the second element with respect to the moles of all the rare earths and said elements, and more particularly in the range 10 ppm to 500 ppm.
8. Borate according to any one of the preceding claims, characterized in that Ln represents yttrium and gadolinium in combination.
9. Borate according to any one of the preceding claims, characterized in that said first element is europium and said second element is terbium.
10. Borate according to any one of the preceding claims, characterized in that Ln represents lanthanum, said first element is thulium and said second element is terbium.



11. Borate according to any one of the preceding claims, characterized in that it is in the form of cubic, parallelepipedal or spherical particles, and in that it has a dispersion index of not more than 0.8.
- 5 12. Precursor composition, characterized in that it is based on boron, one or more rare earths selected from lanthanum, lutetium, yttrium and gadolinium, at least one first element selected from trivalent elements that are capable of capturing electrons and at least one second element selected from europium II and trivalent elements that are capable of capturing holes, and in that it is capable of producing, after calcining, a rare earth borate with formula LnBO_3 , Ln representing said rare earth or earths, said borate also comprising at least one said first element and at least one said second element.
- 10 13. Precursor composition according to claim 12, characterized in that the first element is selected from europium, samarium, thulium and ytterbium and the second element is selected from cerium, terbium, praseodymium, bismuth, lead, antimony, chromium and iron.
- 15 14. Precursor composition according to claim 12 or claim 13, characterized in that it is based on a hydroxyborocarbonate of one of or the said rare earths, a hydroxyborocarbonate of at least one said first element and a hydroxyborocarbonate of at least one said second element.
- 20 15. Process for preparing a rare earth borate according to one of claims 1 to 11, characterized in that a carbonate or hydroxycarbonate of a rare earth and said elements is reacted with boric acid, the reaction medium being in the form of an aqueous solution, and the reaction product is calcined.
- 25 16. Process according to claim 15, characterized in that the reaction medium is formed using water in a weight ratio of water/boric acid + carbonate or hydroxycarbonate of at least 300%, more particularly at least 600%.
17. Process according to claim 15 or 16, characterized in that the reaction is carried out by removing the CO_2 formed in the course thereof.
- 30 18. Process for preparing a precursor composition according to claim 12 or claim 13, characterized in that a carbonate or hydroxycarbonate of at least one said rare earth, at least one said first element and at least one said second element is reacted with boric acid, the reaction medium being in the form of an aqueous solution, and the reaction product is optionally washed and/or dried.
19. Visualization process employing a plasma excitation or X-rays, characterized in that a

borate according to one of claims 1 to 11 is used as the luminophore.

20. Visualization system employing plasma excitation or X-rays, characterized in that it comprises a borate according to one of claims 1 to 11 as the luminophore.

