

RARE-EARTH BORATE AND PRECURSOR THEREOF, PROCESSES
FOR THEIR PREPARATION AND USE OF THE BORATE
AS A LUMINOPHORE

The present invention relates to a rare-earth
5 borate, to a precursor thereof, to processes for their
preparation and to the use of this borate as a
luminophore.

The fields of luminescence and electronics
are currently experiencing a period of considerable
10 development. As an example of such development, mention
may be made of the improvement of plasma systems
(screens and lamps) for novel visualization and
lighting techniques. One concrete application is the
replacement of current television screens with flat
15 screens. These novel applications require luminophoric
materials having increasingly enhanced properties.
Thus, besides their luminescent property, specific
characteristics of morphology or of particle size are
required of these materials in order to facilitate, in
20 particular, their use in the desired applications.

More precisely, there is a requirement for
luminophores having a narrow particle size distribution
and, optionally, in the form of micron-sized
individualized particles.

25 The main object of the invention is to afford
products having such particle size characteristics.

Another object of the invention is to afford

luminophores having enhanced luminescent properties.

A third subject of the invention is a preparation process which makes it possible to obtain products having these characteristics directly.

5 With this aim, the rare-earth borate of the invention is 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.

 By way of borate precursor, the invention
10 also relates to a rare-earth boron hydroxycarbonate, 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.

 As other product, the invention moreover
15 relates, by way of borate precursor, to an yttrium boron hydroxycarbonate also comprising terbium, this compound having luminescent properties.

 The invention also covers a process for the preparation of a rare-earth boron hydroxycarbonate,
20 characterized in that a rare-earth carbonate or hydroxycarbonate is reacted with boric acid, the reaction medium being in the form of an aqueous solution.

 The invention moreover covers a process for
25 the preparation of a rare-earth borate, characterized in that a rare-earth carbonate or hydroxycarbonate is 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 even more fully apparent on reading the description which follows and from the attached drawings, in which:

- Figure 1 is a graph giving the intensity of emission as a function of the wavelength for a europium-doped yttrium borate according to the invention, under excitation at 254 nm;

- Figure 2 is a graph giving the intensity of emission as a function of the wavelength, under the same excitation, for a product of the same formula according to the prior art, prepared by grogging.

Throughout the description, the term rare-earth is understood to refer to the elements of the group consisting of yttrium, scandium and the elements of the Periodic Table of atomic number between 57 and 71 inclusive.

The preparation processes will first be described and the products obtained in the various steps will then be studied in detail.

One characteristic of the processes of the invention is the starting material. A rare-earth carbonate or hydroxycarbonate is used at the start.

It is possible to start with a mixture of carbonates or hydroxycarbonates of different rare-earths or mixed carbonates or hydroxycarbonates of rare-earths. Indeed, the invention applies to borates

of one or more rare-earths or to hydroxycarbonates of boron and of one or more rare-earths. Accordingly, throughout the description, everything which is described regarding a rare-earth borate, a rare-earth boron hydroxycarbonate and regarding processes for their preparation should be understood as applying to the case where several rare-earths are present.

Rare-earth carbonates or hydroxycarbonates are products which are known per se and which may be obtained, for example, by precipitation of one or more rare-earth salts with ammonium carbonate or bicarbonate.

The starting material is reacted with boric acid. The reaction is preferably carried out under hot conditions, for example at a temperature of between 40°C and 90°C.

According to another characteristic of the invention, 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 water/boric acid + carbonate mass ratio is at least 300 %, more particularly at least 1000 %. This ratio may even more particularly be at least 1500 %.

It is possible to work with an excess of boric acid. This excess may be, for example, between 5 mol% and 100 mol% ($[B]/[RE] = 1.05$ to 2, RE=rare-earth).

It may be advantageous to carry out the

reaction while removing the CO_2 formed during the course thereof. This removal may take place, for example, by flushing the reaction medium with a neutral gas such as nitrogen. This variant makes it possible to
5 obtain products of finer particle size.

According to another variant, the reaction is carried out by attacking the rare-earth carbonate or hydroxycarbonate with boric acid in the mother liquors from precipitation thereof. It is advantageous to carry
10 out this attack on a freshly prepared carbonate or hydroxycarbonate. This variant makes it possible to obtain products of spherical morphology.

At the end of the reaction, a precipitate is obtained which is separated from the reaction medium by
15 any known means, for example by filtration, and which is optionally washed and then dried. One of the advantages of the process of the invention is that it makes it possible to obtain a precipitate which may readily be filtered and washed. After drying, an
20 additional washing with a dilute acid, for example nitric acid, may also be carried out in order to remove any traces of carbonate which has not reacted completely.

The rare-earth boron hydroxycarbonate of the
25 invention is thus obtained.

The process for the preparation of the borates of the invention is also characterized in that a rare-earth carbonate or hydroxycarbonate is reacted

with boric acid. The precipitate is recovered after this reaction and everything which has been stated above for this reaction and the treatment of the precipitate also applies here for this first step of the process. The precipitate is then calcined.

This calcination generally takes place at a temperature of between 500 and 1400°C, more particularly between 500 and 1100°C. Given the properties of the hydroxycarbonate precipitate, it is entirely possible to carry out this calcination under air. This is a valuable advantage when compared with the processes of the prior art, which generally require reductive atmospheres. Obviously, it would not be departing from the scope of the present invention to use, for this calcination, a reductive atmosphere (for example hydrogen) or a neutral atmosphere (argon) or mixtures thereof.

After the calcination, a borate according to the invention is obtained.

Another important advantage of the process is that it makes it possible to obtain directly a borate having the desired particle size characteristics. It is not necessary, for example, to carry out grinding in order to arrive at the desired particle size.

The borate of the invention will now be described.

The rare-earth borate of the invention is essentially an orthoborate of formula LnBO_3 , Ln

representing at least one rare-earth.

The first characteristic of this borate is its morphology.

The borate of the invention may be in the form of spherical, cubic or parallelepipedal particles. The term parallelepipedal also covers products in the form of platelets, that is to say, in effect, parallelepipeds which are shorter, or very much shorter, in height than they are long.

These particles may also have a size which varies in wide proportions. According to a preferred embodiment of the invention, the average particle size is not more than 10 μm , more particularly not more than 5 μm , and, even more particularly, it may be between 0.5 and 5 μm .

Throughout the description, the average size and the dispersion index are values obtained by carrying out the technique of laser diffraction, using a granulometer of the Cilas HE 850 type (distribution on a volume basis).

The particles are of homogeneous morphology, that is to say that most of them, and preferably all of them, have this same morphology.

Another characteristic of the borate of the invention is its particle size distribution. This particle size distribution is narrow. Thus, the dispersion index σ/m is not more than 0.8. It may more particularly be not more than 0.7 and even more

particularly not more than 0.6. It is possible, in the context of the present invention, to obtain products having a dispersion index of 0.4 or 0.5.

The term dispersion index is understood to refer to the ratio:

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

in which:

- d_{90} is the particle diameter for which 90 % of the particles have a diameter of less than d_{90} ;
- d_{10} is the particle diameter for which 10 % of the particles have a diameter of less than d_{10} ;
- d_{50} is the average particle diameter.

The diameters are determined by Cilas granulometry (distribution on a mass basis).

The borate of the invention may also be in the form of well-separated and individualized particles. There are few or no particle agglomerates.

Consequently, the borate may be in the form of particles having a size, a dispersion index and a morphology as described above, these particles being substantially whole. The term whole particle is understood to refer to a particle which has not been broken or crushed as is the case during grinding.

Scanning electron microscopy photos make it possible to distinguish crushed particles from particles which have not been crushed.

The rare-earth making up the borate of the invention, that is to say that which forms the product matrix with borate, generally belongs to the group of rare-earths which have no luminescent property. Thus, 5 this rare-earth which makes up the borate may be chosen, alone or in combination, from the group comprising yttrium, gadolinium, lanthanum, lutetium and scandium. More particularly, it may be yttrium and/or gadolinium.

10 The borate may moreover comprise one or more dopants. In a manner which is known per se, the dopants are used in combination with the matrix in order to give it luminescent properties. These dopants may be chosen from antimony, bismuth and rare-earths. In the 15 latter case, the rare-earth(s) used as dopant are chosen from the group of rare-earths with luminescent properties and they are different from the rare-earth making up the borate. As dopant rare-earth, mention may be made of cerium, terbium, europium, thulium, erbium 20 and praseodymium. Terbium and europium are more particularly used. The content of dopant is usually not more than 50 mol% relative to the rare-earth borate matrix ($[\text{dopant}]/[\text{EREBO}_3]$ ratio), ERE representing all the rare-earths and dopants present in the borate. In 25 the particular case of europium and terbium, the contents of these elements are preferably between 5 and 25 % and 5 and 50 % respectively. In the case of thulium, the content of thulium is preferably between

0.1 and 1 %.

According to a particular embodiment, the rare-earth borate of the invention is a borate of at least one element chosen from yttrium, gadolinium, scandium and lutetium. It is characterized in that it comprises europium as dopant and in that it has an emission intensity maximum in the wavelength (λ) range between 600 and 650 nm under excitation at 254 nm. The term emission intensity maximum is understood to mean that the value of the integral of the curve: intensity = $f(\lambda)$ for values of λ from 600 to 650 nm represents the major part of the value of the integral of the same curve for values of λ varying throughout the visible region. Consequently, the borate according to this embodiment is a red luminophore, essentially emitting in this colour, in contrast with the luminophores of the same composition of the prior art which essentially emit in the orange region, that is to say in wavelengths less than 600 nm.

The europium content in the borate of this embodiment is generally not more 50 % calculated as described above.

Lastly, in this embodiment, the rare-earth element is more particularly yttrium and/or gadolinium.

As other embodiments of the invention, mention may be made of cerium-doped gadolinium orthoborate, thulium-doped gadolinium orthoborate, both of pseudo-vaterite structure, and thulium-doped

lanthanum orthoborate of aragonite structure.

By way of precursor of the borates which have just been described, the invention also relates to a rare-earth boron hydroxycarbonate.

5 This hydroxycarbonate is 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.

 This hydroxycarbonate may moreover comprise,
10 as additive, an element which is of the same type as the dopants which have been described above.

 The rare-earth making up the hydroxycarbonate (other than the additive) generally belongs to the group of rare-earths which have no luminescent
15 property. Thus, this rare-earth making up the borate may be chosen from the group comprising yttrium, gadolinium, lanthanum, lutetium and scandium. It may more particularly be yttrium and/or gadolinium.

 Moreover, the characteristics of particle
20 size, morphology, homogeneity and absence of agglomeration which have been mentioned for the borates of the invention are found in the precursors. These precursors may also be in the form of whole particles in the sense given above. Thus, everything which has
25 been described regarding the characteristics of the borates also applies here.

 As other novel precursors, the invention also relates to an yttrium boron hydroxycarbonate and an

yttrium gadolinium boron hydroxycarbonate, both
moreover comprising terbium, which have luminescent
properties in the green region. To the Applicant's
knowledge, no product of this type also having
5 luminophoric properties existed hitherto. For this
precursor, the amount of terbium may be between 5 and
50 %, this amount expressed as before.

Lastly, the latter precursor may also have a
dispersion index of not more than 0.8 and the same
10 cubic, parallelepipedal or spherical morphology as that
described above. It may, here also, have the same
characteristics of particle size, homogeneity and
absence of agglomeration as those of the other
hydroxycarbonates of the invention.

15 On account of their properties, the borates
of the invention and the terbium-doped yttrium boron
hydroxycarbonates described above, or as obtained by
the processes described above, may be used as
luminophores. They may be used, in particular, in low-
20 voltage luminescence, in particular in the manufacture
of any device using this low-voltage luminescence, such
as screens with a field effect. These borates and
hydroxycarbonates moreover have luminescent properties
under electromagnetic excitation in the wavelength
25 range used in plasma systems and in mercury vapour
lamps. Thus, they can be used as luminophores in plasma
systems (visualization screen or lighting system) or in
trichromatic lamps.

Lastly, the invention also relates to luminescent devices, of the type having a screen with a field effect for example, incorporating the borates or hydroxycarbonates described above or as obtained by the processes described above. In these devices, the luminophores are placed on the screens subjected to low-energy excitation. Similarly, the invention relates to plasma systems or to mercury vapour systems in whose manufacture the borates or the hydroxycarbonates may take part. The use of the luminophores in the manufacture of low-voltage luminescence devices or plasma systems takes place according to well-known techniques, for example by silk-screen printing, electrophoresis or sedimentation.

Examples will now be given.

EXAMPLES

Two types of precursors are used for these syntheses: a rare-earth carbonate $\text{Ln}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ and a rare-earth hydroxycarbonate LnOHCO_3 (Ln = rare-earth).

These precursors are used in suspension in water, the carbonate and the hydroxycarbonate having been precipitated beforehand by reaction of ammonium bicarbonate and aqueous ammonia with rare-earth nitrates or co-nitrates, washed and then dried in the oven (50°C).

A solution of boric acid is used as second reactant.

The amount of carbonate is such that the

rare-earth concentration is 0.2 M after the addition of acid.

The amount of boric acid is such that a suitable B/Ln ratio is obtained.

5 The procedure is as follows:

 The suspension of carbonate or of hydroxycarbonate, introduced into the bottom of the reactor tank, is heated to the desired temperature T and stirred vigorously. The boric acid solution is
10 added (introduction time of about 30 min) using a peristaltic pump and the reaction mixture is left stirring for a further two hours counting from the end of the addition. The precipitate obtained is filtered off on a sinter funnel, washed with millipore water and
15 then dried in the oven at 110°C. The powder is finally washed with a sufficient amount of dilute nitric acid in order to remove any traces of carbonate which has not reacted completely.

 The powder obtained is then calcined in a
20 muffle furnace (under air) at 1100°C for two hours.

 All the compounds described hereinbelow have the same crystallographic structure, determined by X-ray diffraction:

 - before calcination: $\text{LnB}(\text{OH})_4\text{CO}_3$ (rare-earth
25 boron hydroxycarbonate, File JCPDS 40-508)

 - after calcination: LnBO_3 (orthoborate of pseudo-vaterite structure, JCPDS 16-277).

 In the examples, the particle size was

determined according to the abovementioned Cilas technique. It is further pointed out that the measurement was made on a dispersion of the product in aqueous 0.05 % by weight sodium hexametaphosphate solution which had previously been subjected to passage with an ultrasound probe (probe with an end piece 13 mm in diameter, 20 KHz, 120 W) for 3 minutes.

Examples 1 to 4 which follow relate to the synthesis of europium-doped yttrium orthoborate YBO_3 .

10 EXAMPLE 1

The precursor used is a mixed carbonate of yttrium and of europium. The final composition aimed at is $\text{Y}_{0.9}\text{Eu}_{0.1}\text{BO}_3$.

The attack temperature $T = 70^\circ\text{C}$ and the ratio
15 $[\text{B}]/[\text{Ln}] = 1.5$.

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of 2 μm and a dispersion index $\sigma/m = 0.6$.

20 After calcination, the morphology and the size are conserved but with a slightly higher dispersion index $\sigma/m = 0.7$.

Figure 1 is a graph giving the emission intensity as a function of the wavelength for this
25 borate under excitation at 254 nm.

EXAMPLE 2

Example 1 is repeated, but with an attack temperature of 90°C .

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of 5 μm and a dispersion index $\sigma/m = 0.4$.

5 After calcination, the morphology is entirely conserved ($\sigma/m = 0.4$).

EXAMPLE 3

The precursor used is a mixed hydroxycarbonate of yttrium and of europium. The final
10 composition aimed at is $\text{Y}_{0.9}\text{Eu}_{0.1}\text{BO}_3$.

The attack temperature is 70°C and the ratio [B]/[Ln] is 1.05.

Characteristics:

Before calcination, the product is in the
15 form of small cubes with an average Cilas diameter of 3 μm and a dispersion index $\sigma/m = 0.5$.

After calcination, the morphology and the particle size remain unchanged but the dispersion index is 0.6.

20 EXAMPLE 4

Example 3 is repeated, but with an attack temperature of 40°C.

Characteristics:

Before calcination, the product is in the
25 form of small cubes with an average Cilas diameter of 1 μm and a dispersion index $\sigma/m = 0.6$.

After calcination, the morphology remains unchanged but the dispersion index is 0.7.

EXAMPLE 5

This example relates to the synthesis of a
5 europium-doped mixed orthoborate of yttrium and of gadolinium (YGd)BO₃.

The precursor used is a mixed carbonate of yttrium, of gadolinium and of europium. The final composition is Y_{0.45}Gd_{0.45}Eu_{0.1}BO₃.

10 The attack temperature is 70°C and the stoichiometric ratio [B]/[Ln] used is 1.05.

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of
15 1.5 μm and a dispersion index σ/m = 0.5.

After calcination, the morphology and the size are unchanged (σ/m = 0.5).

EXAMPLE 6

This example relates to the synthesis of a
20 terbium-doped yttrium orthoborate YBO₃.

The precursor used is a mixed carbonate of yttrium and of terbium. The final composition aimed at is Y_{0.8}Tb_{0.2}BO₃.

The attack temperature is 70°C and the
25 stoichiometric ratio [B]/[Ln] used is 1.5.

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of 1.5 μm and a dispersion index $\sigma/m = 0.7$. This product has the characteristic feature of being luminescent in the green region directly after drying at 110°C.

After calcination, the morphology remains unchanged ($\sigma/m = 0.7$).

EXAMPLE 7

This example relates to the synthesis of a terbium-doped mixed orthoborate of yttrium and of gadolinium (YGdBO_3).

The precursor used is a mixed carbonate of yttrium, of gadolinium and of terbium. The final composition aimed at is $\text{Y}_{0.4}\text{Gd}_{0.4}\text{Tb}_{0.2}\text{BO}_3$.

The attack temperature is 70°C and the stoichiometric ratio $[\text{B}]/[\text{Ln}]$ used is 1.5.

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of 1.5 μm and a dispersion index $\sigma/m = 0.6$. This product has the characteristic feature of being luminescent in the green region directly after drying at 110°C.

After calcination, the morphology and the size are unchanged but the dispersion index σ/m is equal to 0.7.

EXAMPLE 8

This example relates to the synthesis of a gadolinium orthoborate doped with cerium and praseodymium.

The precursor used is a mixed carbonate of gadolinium, cerium and praseodymium. The final composition aimed at is $\text{Gd}_{0.9}\text{Ce}_{0.05}\text{Pr}_{0.05}\text{BO}_3$.

The attack temperature is 70°C and the stoichiometric ratio $[\text{B}]/[\text{Ln}]$ used is 1.5.

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of 4 μm and a dispersion index $\sigma/m = 0.5$.

EXAMPLE 9

This example relates to the synthesis of a gadolinium orthoborate doped with cerium and terbium.

The precursor used is a mixed carbonate of cerium, gadolinium and praseodymium.

The final composition aimed at is $\text{Ce}_{0.3}\text{Gd}_{0.5}\text{Tb}_{0.2}\text{BO}_3$.

The attack temperature is 70°C and the stoichiometric ratio $[\text{B}]/[\text{Ln}]$ used is 1.5.

Characteristics:

Before calcination, the product is in the form of small cubes with an average Cilas diameter of 4 μm and a dispersion index $\sigma/m = 0.5$.

EXAMPLE 10

Example 1 is repeated, but the attack is carried out while flushing with nitrogen so as to remove the CO_2 formed during the reaction more quickly. The particles obtained are of finer particle size than in the absence of flushing.

Characteristics:

Before calcination, the product is in the form of small parallelepipedal grains with an average Cilas diameter of $1\text{ }\mu\text{m}$ and a dispersion index $\sigma/m = 0.7$.

After calcination, the morphology is conserved. The average Cilas diameter changes to $1.5\text{ }\mu\text{m}$ whereas the dispersion index remains unchanged ($\sigma/m = 0.7$).

15 EXAMPLE 11

The same product as that of Example 1 is prepared, but the mode of synthesis consists in attacking a mixed carbonate of yttrium and of europium (freshly precipitated) directly in the mother liquors from precipitation. Boric acid in crystalline form is then added thereto and the mixture is heated at 70°C with stirring (2 hours). The rest of the process is identical to the general procedure.

Characteristics:

25 Before and after calcination, the product is in the form of small spheres with an average Cilas diameter of about one micron and are very monodisperse

($\sigma/m = 0.5$).

EXAMPLE 12

This example relates to the synthesis of a cerium-doped gadolinium orthoborate GdBO_3 .

5 The precursor used is a mixed carbonate of gadolinium and of cerium. The final composition is $\text{Gd}_{0.95}\text{Ce}_{0.05}\text{BO}_3$.

The attack temperature is 70°C and the stoichiometric ratio $[\text{B}]/[\text{Ln}]$ used is 1.5.

10 Characteristics:

Before calcination at 1100°C under air, the product is in the form of small cubes with an average Cilas diameter of $2.2 \mu\text{m}$ and a dispersion index $\sigma/m = 0.6$.

15 After calcination, the morphology remains unchanged. The product has a pseudo-vaterite structure.

EXAMPLE 13

This example relates to the synthesis of a thulium-doped lanthanum orthoborate LaBO_3 .

20 The precursor used is a mixed carbonate of lanthanum and of thulium. The final composition is $\text{La}_{0.99}\text{Tm}_{0.01}\text{BO}_3$.

The process is carried out as in Example 12.

Characteristics:

25 Before calcination, the product is in the form of slightly agglomerated platelets with an average

Cilas size of 4.8 μm and a dispersion index $\sigma/m = 0.75$.

After calcination at 1100°C under air, the morphology remains unchanged.

EXAMPLE 14

5 This example relates to the synthesis of a thulium-doped gadolinium orthoborate GdBO_3 .

The precursor used is a mixed carbonate of gadolinium and of thulium. The final composition is $\text{Gd}_{0.99}\text{Tm}_{0.01}\text{BO}_3$.

10 The attack temperature is 70°C and the stoichiometric ratio $[\text{B}]/[\text{Ln}]$ used is 1.5.

Characteristics:

Before calcination, the product has an average Cilas diameter of 2.1 μm and a dispersion index
15 $\sigma/m = 0.6$. After calcination at 1100°C under air, the morphology remains unchanged.

CLAIMS

1. Rare-earth borate, characterized in that it is in the form of cubic, parallelepipedal or spherical particles and in that it has a dispersion
5 index of not more than 0.8.

2. Borate according to claim 1, characterized in that it moreover comprises, as dopant, at least one element chosen from antimony, bismuth and rare-earths other than that making up the borate, it
10 being possible for the dopant rare-earth more particularly to be cerium, terbium, europium, thulium, erbium and praseodymium.

3. Borate according to either of the preceding claims, characterized in that the rare-earth
15 making up this borate belongs to the group comprising yttrium, gadolinium, lanthanum, lutetium and scandium.

4. Borate of at least one element chosen from yttrium, gadolinium, scandium and lutetium according to one of the preceding claims, characterized
20 in that it comprises europium as dopant and in that it has an emission intensity maximum in the wavelength range between 600 and 650 nm under excitation at 254 nm.

5. Borate according to the preceding claim,
25 characterized in that the abovementioned element is yttrium and/or gadolinium.

6. Borate according to one of the preceding claims, characterized in that it has an average

particle size of not more than 10 μm .

7. Borate according to one of the preceding claims, characterized in that it has a content of dopant element of not more than 50 mol%.

5 8. Rare-earth boron hydroxycarbonate, 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.

9. Hydroxycarbonate according to claim 8,
10 characterized in that it moreover comprises at least one element chosen from antimony, bismuth and rare-earths other than that making up the hydroxycarbonate.

10. Hydroxycarbonate according to claim 8 or 9, characterized in that the rare-earth making up this
15 hydroxycarbonate belongs to the group comprising yttrium, gadolinium, lanthanum, lutetium and scandium.

11. Yttrium boron hydroxycarbonate or yttrium gadolinium boron hydroxycarbonate, also comprising terbium, having luminescent properties.

20 12. Hydroxycarbonate according to claim 11, characterized in that it has a dispersion index of not more than 0.8.

13. Hydroxycarbonate according to claim 11 or 12, characterized in that it is in the form of
25 cubic, parallelepipedal or spherical particles.

14. Process for the preparation of a rare-earth boron hydroxycarbonate, characterized in that a rare-earth carbonate or hydroxycarbonate is reacted



with boric acid, the reaction medium being in the form of an aqueous solution.

15. Process for the preparation of a rare-earth borate, characterized in that a rare-earth carbonate or hydroxycarbonate is reacted with boric acid, the reaction medium being in the form of an aqueous solution, and the reaction product is calcined.

16. Process according to claim 14 or 15, characterized in that the reaction medium is formed using water in a water/boric acid + carbonate mass ratio of at least 300 %, more particularly of at least 1000 %.

17. Process according to claim 14, 15 or 16, characterized in that the reaction is carried out while removing the CO₂ formed.

18. Process according to one of claims 15 to 17, characterized in that calcination is carried out at a temperature between 500 and 1100°C, preferably under air.

19. Process according to one of claims 14 to 18, characterized in that boric acid is reacted with the rare-earth carbonate or hydroxycarbonate in the mother liquors thereof.

20. Use, as a luminophore, of a borate according to one of claims 1 to 7 or of a borate obtained by the process according to one of claims 15 to 19 or of a hydroxycarbonate according to one of claims 11 to 13.



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REPLACED

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21. Use, as a luminophore in low-voltage luminescence in plasma systems or in trichromatic lamps, of a borate according to one of claims 1 to 7 or of a borate obtained by the process according to one of
5 claims 15 to 19 or of a hydroxycarbonate according to one of claims 11 to 13.

22. Device using low-voltage luminescence, characterized in that it comprises a borate according to one of claims 1 to 7 or a borate obtained by the
10 process according to one of claims 15 to 19 or a hydroxycarbonate according to one of claims 11 to 13.

23. Plasma system, characterized in that it comprises a borate according to one of claims 1 to 7 or a borate obtained by the process according to one of
15 claims 15 to 19 or a hydroxycarbonate according to one of claims 11 to 13.

24. Trichromatic lamp, characterized in that it comprises a borate according to one of claims 1 to 7 or a borate obtained by the process according to one of
20 claims 15 to 19 or a hydroxycarbonate according to one of claims 11 to 13.

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