

The present invention concerns a process for the production of rare earth and ammonium double oxalates, their use in the production of rare earth oxides and to the products obtained.

5 It particularly concerns a process for the production of double oxalates with a fixed morphology and granulometry.

Rare earth oxides have numerous applications, particularly in the fields of ceramics and electronics. Currently, however,
10 the demand for products with a controlled grain size is increasing.

One conventional method of producing rare earth oxides is widely described in the literature, particularly in NOUVEAU
15 TRAITE DE CHIMIE MINERALE, Vol VII, (1959), p 1007, by Paul PASCAL. It involves calcining rare earth oxalates, produced by precipitation of aqueous solutions of rare earth salts with oxalic acid, between 500°C and 900°C. However, this process can only produce rare earth oxides with a large grain size.

20 Japanese patent JP-53 095911-A (Chemical Abstracts 90, 40940 w) describes the preparation of fine rare earth oxides, in particular fine yttrium oxide, by calcining an oxalate of yttrium and ammonium, consisting in precipitating yttrium
25 hydroxide from an aqueous solution of an yttrium salt, by reacting the aqueous yttrium salt solution with a basic aqueous solution such as ammonia, then treating the resulting hydroxide slurry with oxalic acid, and finally separating out the precipitate obtained, washing it then calcining it at a
30 temperature of 750°C. That process, according to the description in JP 53-095911-A, produces fine yttrium oxide. The particle diameter is between 0.9 and 4.5 μm , the crystals forming platelets with rounded edges.

35 The paper in Bull Chem Soc Japan vol 63, pp 378-82 (1990) describes a conventional double oxalate preparation process in which an aqueous ammonia solution is introduced into an yttrium oxalate solution.

However, the particle dimensions are still relatively large compared with the dimensions required in some applications, such as luminescence. In addition, controlling particle dimensions is relatively difficult since the operating conditions of the process influence them strongly.

The present invention aims to overcome these problems in providing a process for the production of rare earth and ammonium double oxalates having a narrow grain size distribution, with average crystal diameters which can be less than a micron.

The term "rare earth and ammonium double oxalate" means a compound containing one or more rare earths which, after calcining, produces simple or mixed oxides.

The invention thus provides a process for the production of a rare earth and ammonium double oxalate, characterised in that it consists in:

- adding a second solution containing a rare earth compound to a first solution containing oxalate and ammonium ions;
- separating the precipitate obtained; and
- drying if required.

The rare earth compound is advantageously a soluble compound such as a rare earth salt.

Examples of suitable salts are the chlorides, nitrates, sulphates or acetates of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thulium, ytterbium, lutetium or a mixture thereof. In particular, an aqueous solution containing rare earth salts which are directly or indirectly derived from the treatment of rare earth minerals may be used.

While the process is suitable for ceric rare earths, it is particularly suitable for yttric rare earths.

The term "ceric rare earths" means the lightest rare earth elements in terms of atomic number, starting with lanthanum and extending to neodymium, and the term "yttric rare earths" means the heaviest rare earth elements in terms of atomic number, starting with samarium and extending to lutetium, including yttrium.

The rare earth compound concentration is not critical.

The second solution is an aqueous solution in which the pH can be adjusted to a particular value or to a particular zone by addition of a buffer solution or acids if required. In general, the second solution contains mainly one or more rare earth compounds.

Examples of acids are mineral acids such as nitric acid.

The first solution contains ammonium and oxalate ions in the form of one or more salts containing the two species, such as ammonium oxalate or ammonium tetraoxalate, or by a mixture of compounds each contributing one of the ammonium or the oxalate species. Examples of compounds contributing the ammonium ion are ammonium salts such as ammonium nitrate or chloride, or ammonia, as a gas or in solution.

The oxalate species can be supplied by metal oxalates such as sodium oxalate, or preferably by oxalic acid.

The concentration of $(C_2O_4)^=$ and NH_4^+ ions in the solution is not critical and can vary between large limits.

In a preferred embodiment, the ammonium and oxalate concentrations and the rare earth concentration in the second solution is determined, along with the volumes of the first and second solutions, to produce a molar ratio between the oxalate ion and the rare earths $((C_2O_4)^=/RE)$, following addition, greater than or equal to 2, advantageously greater

than 2.5, and a ratio of ammonium to rare earths (NH_4^+/RE) greater than or equal to 2, preferably greater than 2.5.

5 In one embodiment of the invention, the first solution is an ammonium oxalate solution.

10 In a further embodiment of the invention, the first solution is a solution of ammonium oxalate and oxalic acid. Advantageously, the $(\text{C}_2\text{O}_4)^{=}/\text{NH}_4^+$ is greater than 2 and between 2 and 4.

15 In a still further embodiment of the invention, the first solution is a solution of ammonium oxalate and ammonia, and the $(\text{C}_2\text{O}_4)^{=}/\text{NH}_4^+$ molar ratio is greater than 0, advantageously between 0.4 and 2.

20 The first solution can also comprise a mineral acid (HA) such as nitric acid. This acid can be added to an ammonium oxalate solution or liberated in situ by addition of oxalic acid to an ammonium salt solution, for example ammonium nitrate.

25 When a mineral acid HA is present in the first or second solution, the quantity of acid HA used is calculated so as to produce a molar ratio of anion A^- of said acid with respect to the total quantity of oxalate of less than 5.

30 The operating conditions of the process are not critical for double oxalate production. However, controlling the rate of introduction of the second solution, the temperature and the stirring conditions in the mixture means the morphology of the precipitated double oxalate can be controlled.

35 The process of the invention can be operated continuously by continuous mixing of the first and second solutions described above.

In addition, the temperature affects the precipitation yield since the solubility coefficient of the double oxalate increases with increasing temperature.

5 The precipitate obtained is separated from the supernatant liquid by any solid/liquid separation process, for example filtration, centrifuging, decanting or an analogous process. It can also be washed one or more times, for example to eliminate the soluble salts.

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The rare earth and ammonium double oxalate can be dried to evaporate the free water, for example by heat treatment between 50°C and 100°C or drying at reduced pressure.

15 The rare earth and ammonium double oxalate obtained by the process of the invention is constituted by particles whose shape and dimensions depend on the nature and pH of the solutions as well as on the conditions of temperature, stirring and rate of introduction used during mixing of the
20 solutions.

Thus, when the first solution is a solution of ammonium oxalate, the product obtained is constituted by particles in the form of thin platelets (about 0.3 μm thick) and average
25 dimensions of between 0.5 μm and 3 μm , advantageously between 0.5 μm and 1 μm .

When the first solution is a solution of a mixture of oxalic acid and ammonia, or another ammonium compound with the
30 exception of ammonium oxalate, the average particle dimension is between 1 μm and 5 μm . These particles are substantially cubic in form.

the process of the invention can produce a rare earth and
35 ammonium double oxalate with homogeneous granulometry. Thus the grain size distribution of the crystals is very narrow. The dispersion coefficient of crystal size is generally less than 0.7, advantageously between 0.2 and 0.6.

The term "dispersion coefficient" means the ratio $\frac{\theta_{84} - \theta_{16}}{2\theta_{50}}$

5 where θ_{84} , θ_{16} and θ_{50} represent the diameters of particles corresponding to 84%, 16% and 50% thereof.

One use of these rare earth and ammonium double oxalates is in the production of rare earth oxides by thermal decomposition.

10 The morphology and granulometry of the rare earth oxides obtained by decomposition of a double oxalate is generally similar to that of the double oxalate precursor. However, depending on the heat treatment conditions for the double oxalate, the granulometry of the oxide can be slightly
15 different to that of the oxalate.

Heat treatment or calcining is generally carried out at a temperature of between 600°C and 1200°C, advantageously between 800°C and 1000°C.

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The calcining period is conventionally determined by heating to constant weight. As an example, the calcining period can be between 30 minutes and about 6 hours.

25 The following examples are given by way of indication and illustrate the invention.

EXAMPLE SERIES I

30 A solution of 170 g/l of yttrium nitrate, expressed as Y_2O_3 , was added to different ammonium oxalate solutions with concentrations of less than 0.9 M.

The tests carried out are summarised in Table 1 below.

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The size and grain size distribution of the products obtained were determined using a SEDIGRAPH 5000D which determined the sedimentation rate of suspended particles and determined the grain size distribution as a cumulative percentage as a

function of equivalent spherical diameters. This determination was based on STOKES' law.

NH ₄ /Y ratio	[Y] gY ₂ O ₃ /l (l)	D ₅₀ μm	Grain size dispersion coefficient
5	5	0.69	0.57
5	17	0.84	0.47
6	17	0.80	0.35
8	17	0.64	0.53

where [Y] : total yttrium concentration in the reaction medium, expressed as Y₂O₃;

D₅₀ : average dimension of the rare earth oxide obtained by calcining the double oxalate (900°C for 1 hour).

The particles were in the form of platelets with fairly irregular contours.

EXAMPLE SERIES II

This series of examples was carried out using an yttrium nitrate second solution which was identical to that of the first series, with a first solution containing a mixture of (NH₄)₂C₂O₄ and H₂C₂O₄.

The results and ratios between the species used are summarised in Table II. The concentration of Y in the reaction medium was 17 g/l of Y₂O₃.

C ₂ O ₄ ⁼ /Y	NH ₄ ⁺ /Y	D ₅₀ oxide	Grain size dispersion coefficient (F)
2.5	2.5	0.90	0.46
3.0	3.0	1.15	0.67
4.0	5.0	1.1	0.40

The double oxalate crystals obtained were in the form of platelets about 0.3 μm thick with average dimensions of 0.7 μm

and 1 μm . The morphologies of the oxalate and calcined oxide are shown in Figures 1 and 2 respectively.

EXAMPLE SERIES III

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These examples were identical to those of series II, this time using a first solution containing ammonia and oxalic acid.

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The results and ratios between the species are given in Table III (final yttrium concentration: 17 g/l of Y_2O_3).

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$\text{C}_2\text{O}_4^{2-}/\text{Y}$	NH_4^+/Y	D_{50} oxide	Grain size dispersion coefficient (F)
4.0	3.0	1.5	0.37
2.5	5.0	0.75	0.47

EXAMPLE IV

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A solution of yttrium nitrate containing 150 g/l expressed as Y_2O_3 and 0.8 mole/l of nitric acid was added to a 25 g/l solution of ammonium oxalate. The quantity of solution used was calculated so as to obtain a ratio between ammonium oxalate and the rare earth salt of greater than 10% of the stoichiometric ratio.

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After separating, drying and calcining the ammonium and yttrium oxalate, an yttrium oxide was obtained with a D_{50} of 2 μm and a grain size dispersion index (F) of 0.5.

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EXAMPLE V

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Example IV was repeated. However, the yttrium nitrate solution contained no nitric acid. The ammonium oxalate solution, however, contained 0.2 mole/l of HNO_3 .

The yttrium oxide obtained following calcining of the ammonium and yttrium oxalate had a D_{50} of 2.3 μm and a grain size dispersion index of 0.45.

EXAMPLE SERIES VI

Example I was repeated using a soluble rare earth salt solution containing 170 g/l of RE_2O_3 , of which 148 g/l was yttrium nitrate and 22 g/l was lanthanum nitrate (La_2O_3).

The solution for precipitation contained 25 g/l of ammonium oxalate.

The quantities of solutions used were calculated so as to produce a NH_4/RE molar ratio of 4.

The precipitate obtained was a double oxalate of yttrium, lanthanum and ammonium.

After calcining at 900°C , a mixed lanthanum and yttrium oxide was obtained containing 12.6% of La_2O_3 , the characteristics of which are shown in the Table below.

NH_4/Y ratio	$[\text{RE}]$ g/l (RE_2O_3)	D_{50} μm	Grain size dispersion coefficient (F)
4	10	0.85	0.68
4	40	0.9	0.70

EXAMPLE VII

A double oxalate of ammonium was prepared by continuous mixing of a 170 g/l yttrium nitrate solution (expressed as Y_2O_3) with a 25 g/l ammonium oxalate solution.

The NH_4/Y ratio was thus 4.75 and the final Y_2O_3 concentration was 16 g/l.

The precipitate recovered after separation and washing was an yttrium and ammonium double oxalate with an average particle diameter of 1.4 μm and a grain size dispersion coefficient (F) of 0.4.



CLAIMS

1. A process for the production of a rare earth and ammonium double oxalate, characterised in that it consists in:
 - adding a second solution containing a rare earth compound to a first solution containing oxalate and ammonium ions;
 - separating the precipitate obtained; and
 - drying if required.
2. Process according to claim 1, characterised in that the first solution is an ammonium oxalate solution.
3. Process according to claim 1, characterised in that the first solution is a solution of oxalic acid and an ammonium compound.
4. Process according to claim 3, characterised in that the ammonium compound is selected from the group comprising ammonia, ammonium oxalate, an ammonium salt of a mineral acid, or a mixture thereof.
5. Process according to claim 4, characterised in that the ammonium salt is an ammonium nitrate or chloride.
6. Process according to claims 2 to 5, characterised in that the first solution contains a mineral acid (HA).
7. Process according to any one of the preceding claims, characterised in that the second solution contains a soluble rare earth salt selected from the group formed by nitrates, chlorides and sulphates, or a mixture of rare earth salts.
8. Process according to any one of claims 1 to 7, characterised in that the second solution comprises a mineral acid (HA).



9. Process according to claim 7 or claim 8, characterised in that the second solution is a solution of yttrium nitrate, europium nitrate, lanthanum nitrate, neodymium nitrate, or dysprosium, cerium, gadolinium or terbium nitrate, or a mixture thereof.
10. Process according to any one of the preceding claims, characterised in that the $C_2O_4^{=}/RE$ and NH_4^+/RE molar ratio following precipitation is greater than 2, preferably greater than 2.5.
11. Process according to any one of the preceding claims, characterised in that the $(C_2O_4)^{=}/NH_4^+$ molar ratio in the first solution is less than 4 and greater than 0.
12. Process according to claim 6 or claim 8, characterised in that the quantity of mineral acid (HA) in the first solution or the second solution is determined so that the ratio between the anion A^- and the oxalate ions in the reaction mixture following mixing is less than 5.
13. Process according to any one of claims 1 to 12, characterised in that it consists in mixing the first and second solutions in a continuous process.
14. A process for the production of rare earth oxides, characterised in that it consists in calcining the ammonium and rare earth double oxalate obtained in accordance with any one of the preceding claims, following drying if required.
15. Process according to claim 14, characterised in that the calcining temperature is between $600^\circ C$ and $1200^\circ C$, preferably between $800^\circ C$ and $1000^\circ C$.
16. An ammonium and rare earth double oxalate, characterised in that it is crystallized in the form of platelets with



an average dimension of between 0.5 μm and 3 μm and a grain size dispersion coefficient of less than 0.7.

- 5 17. A rare earth oxide, characterised in that it is constituted by particles in platelet form with an average dimension of between 0.5 μm and 3 μm with a grain size dispersion coefficient of less than 0.7.