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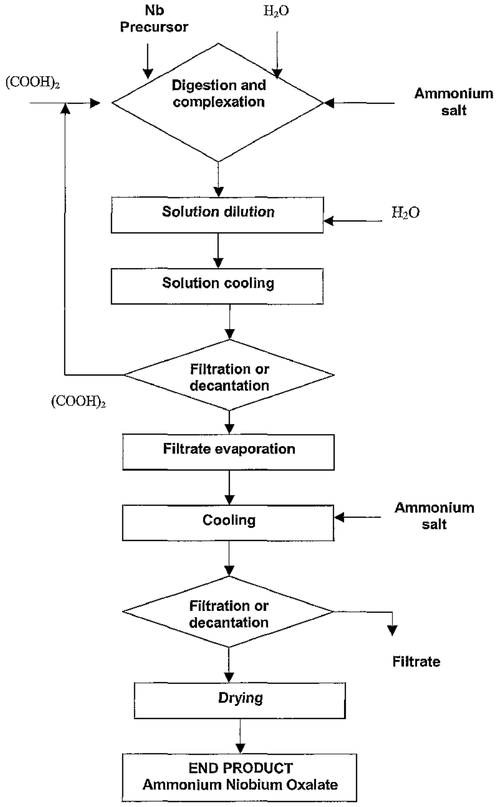
(54) Title: PROCESS OF PRODUCTION OF AMMONIUM NIOBIUM OXALATE, AMMONIUM NIOBIUM OXALATE AND USE OF THE SAME



(57) Abstract: TThe present invention relates to a process of production of ammonium niobium oxalate, to the ammonium niobium oxalate produced by said process that presents high purity, monoclinic crystal structure, Nb content in the range from 10 to 30% by weight, which is stable in contact with air at room temperature, and does not show polymerization by aging, is soluble in water, with a solubility in the range from 60 to 160 grams of niobium per liter of water, at temperatures from 20 to 80°C, and to the use of the same as a niobium precursor, suited to the synthesis of functionalized materials such as ceramic, optical lenses, catalysts, high purity niobium oxides, thin films and crystals, in a macrometric to nanometric range, by preparation methods such as sol-gel, precipitation, deposition, impregnation and decomposition, wherein the niobium is the main constituent or is added to the composition as promoter or dopant.

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"PROCESS OF PRODUCTION OF AMMONIUM NIOBIUM OXALATE, AMMONIUM NIOBIUM OXALATE AND USE OF THE SAME"

FIELD OF THE INVENTION

The present invention relates to a process of production of ammonium niobium oxalate, to an ammonium niobium oxalate produced by said process which presents high purity, monoclinic crystal structure, a Nb content in the range from 5 to 30% by weight, which is stable in contact with air at room temperature, without any polymerization in an aging process, soluble in water, whose solubility is in the range from 60 to 160 grams of niobium per liter of water, at temperatures from 20 to 80°C, and to the use of the same as a niobium precursor, appropriate to the synthesis of functionalized materials such as ceramic, optical lenses, catalysts, high purity niobium oxides, thin films and crystals, in macrometric to nanometric range, by preparation methods such an as sol-gel, precipitation, deposition, impregnation and decomposition, wherein niobium is the main constituent or is added in the composition as a promoter or a dopant.

BACKGROUND OF THE INVENTION

The early testes in an attempt of synthesizing a compound of niobium oxalate were made by F. Russ [F, Russ, Zeitschrift fur Anorganische Chemie, 31 (1902) 42], who synthesized a solid of ammonium, sodium, potassium, rubidium and barium oxalateniobate, of which the presented molecular formula is $M_3[NbO(C_2O_4)_3]nH_2O$, where M is a monovalent metal. In the process described by Russ, the end product shows contaminations of Na, K, Rb and Ba, and this renders this product, a salt which is mixed and of low purity. Lapitskii et al. [L. G. Vlasov, A. V. Lapitskii, M. A. Salimov and B. V. Strizhkov; The Strucutre of Oxalate-complexes of Niobium, Russian Journal of Inorganic Chemistry, vol 7, n° 11 (1962) 1314] synthesized a niobium oxalate complex by mixing hydrated niobium oxide, oxalic acid and ammonium hydroxide, in the proper proportions. The constituents were digested by a hydro treatment process [described by G. W. Morey, Journal of The American Ceramic Society, 36 (1953) 279] and then the solution was evaporated, dried and the solid was ground. According to Lapitskii, the solid formed presented the following molecular formula $(NH_4)_3[NbO(C_2O_4)_3].2H_2O$. The process described by Lapitskii et al presents the drawback of grinding, which generates oxalate based gases, which are toxic. Further, the ammonium niobium oxalate produced by this process ages quickly, becoming insoluble in water.

The process of aging the ammonium niobium oxalate is similar to the olation process occurred for the oxide, as Hughes [M. A. Hughes, Thermal Studies on Niobium Compounds, Journal of Less-Common Metals, 6 (1964) 232] describes. The aging is derived from the loss of water molecules, due to the polymerization between the metal ion and group OH.

Svensson et al. [L. Eriksson, G. Svensson and V. Tabachenko, Crystal Structure of Ammonium Diaquadioxalateoxoniobate(V) Dihydrate, Acta Chemica Scandinavica, 47 (1993) 1038] studied the crystal structure of an ammonium niobium oxalate. According to Svensson, the formula of the ammonium niobium oxalate is $NH_4[NbO(C_2O_4)_2(H_2O)_2].(H_2O)_2$. The study of Svensson et al demonstrated a more probable formulation of the ammonium niobium oxalate, however the water content is in a very restricted range. JCPDS-

International Centers for Diffraction Data published in the year 2000 a record, 83-1993, containing the structure (monoclinic), chemical formula and the data of X-ray diffraction of the Ammonium Niobium Oxide Oxalate Hydrate $[NH_4(NbO(C_2O_4)_2(H_2O)_2.(H_2O)_3]$.

Niobium precursors are necessary to the synthesis of functionalized materials in that niobium is the main constituent or it is added in the composition as promoter or dopant. The different niobium precursors, extensively mentioned in the literature are pentachlorides, niobates, oxalates, tartrates, citrates, niobic acid, alkoxides of the type niobium etoxide and butoxide and similar. Some of these products need special care in handling, such as a controlled and without moisture atmosphere, others present solubility in organic solvents. Few compounds are soluble in water, others can generate, upon being decomposed, gases and toxic substances, frequently rendering production and use of these niobium precursors in industrial scale unfeasible.

Another relevant aspect is the process of industrial production of the niobium precursor, which for many of the above mentioned precursors use raw materials that require care in storage, handling and use due to the impact caused in the environment and of occupational health, thus generating costs in the monitoring and treatment of wastes as well as in the control of the exposition level and of protection equipment for the people involved in the productive process. Therefore, the need of producing a niobium precursor in which the raw materials for production are environmentally sustained and in which the resulting product presents good water solubility, enabling the use thereof in aqueous solutions, is essential for the industrial activity of synthesis of functionalized materials containing niobium in its composition.

In accordance with patent US 6.036.880 ("Niobium-containing aqueous solution for use in producing niobium-containing oxide-catalyst"), the knowledge of the nature of the niobium precursor such as chemical composition and molecular formula as well as the correct preparation of the solution of the niobium precursor in the synthesis process of niobium-containing catalysts is fundamental to correlate the properties and performance the catalyst with the composition of the niobium precursor. According also to this patent, the literature is full of examples with results difficult to be reproduced, materials that present low performances and most importantly, that are not feasible in a commercial scale.

Therefore, the present invention seeks to solve the aforementioned problems through a process of production of ammonium niobium oxalate that uses raw materials environmentally sustained, wherein the product presents high purity, monoclinic crystal structure, specific and controlled Nb contents, which is stable in contact with air at room temperature, which is not subject to polymerization in aging process, is water soluble, thus allowing the use thereof as a niobium precursor, appropriate to the synthesis of functionalized materials such as ceramic, optical lenses, catalysts, high purity niobium oxides, thin films and crystals.

SUMMARY OF THE INVENTION

The present invention relates to a process of producing ammonium niobium oxalate, their characteristics and properties as well as the use thereof as niobium precursor in the synthesis of functionalized materials.

The production process comprises the combination of several unitary operations, of which the steps are: opening or digestion of a precursor niobium compound with oxalic acid and ammonium salt; dilution of the opening solution; cooling for crystallization and precipitation of the oxalic acid in excess; filtration for removal of the precipitated oxalic acid; recycling of the oxalic acid; evaporation of the filtrate to an optimal density of the solution; addition of a new amount of an ammonium salt; cooling for crystallization and precipitation of the ammonium niobium oxalate; filtration for removal of the precipitated ammonium niobium oxalate; and final drying of the ammonium niobium oxalate.

The opening or digestion of a niobium precursor compound with oxalic acid and ammonium salt, in the presence of deionized water as solvent, is accomplished under stirring in a vitrified reactor at a temperature and pressure ensuring the complete solubilization and formation of a solution of anions of niobium oxalate and cations ammonium. Different niobium precursor compounds can be used, and they are selected from, but being not restricted only to these, niobium pentoxide, hydrated niobium oxide, potassium niobate, sodium niobate, fluoro-potassium niobate, fluoro sodium niobate, niobium sulfate or niobium hydroxide. The ammonium salt used is selected among, but not restricted to these only, ammonium oxalate, chloride, acetate, hydroxide or nitrate.

The dilution of the opening solution is made by the addition of deionized water and has as object to reduce the density of the opening solution and to cool the solution to temperatures close to ambient. Cooling of the solution follows for the crystallization and precipitation of the oxalic acid in excess, which did not react with the niobium precursor compound in the formation of the anions of niobium oxalate. The solution, with the resulting precipitate, is then filtered for removal of oxalic acid in excess. Oxalic acid is then recycled, and is used as raw material for the preparation of the next opening solution.

The evaporation of the filtrate is the next step of the process, which has as object to concentrate the solution until this reaches an optimal density. The density is a parameter that determines the efficiency of the process. This step is accomplished under atmospheric pressure or under vacuum, and the temperature of the evaporation is related to the selected work pressure. Once reached the optimal density of the filtrate solution during evaporation, this is then cooled to a temperature close to ambient and then a new amount of ammonium salt is added thereto. The ammonium salt used is selected among, but not to these only, ammonium oxalate, chloride, acetate, hydroxide or nitrate. The addition of the ammonium salt in this step of the process has the purpose of reintroducing ammonium ions in the solution, due to the loss by evaporation, for the formation of the ammonium niobium oxalate as well as to prevent the polymerization of the end product by aging, thus resulting in a water insoluble product. A further cooling at temperature lower than ambient is then carried out for the crystallization and precipitation of the ammonium niobium oxalate, following filtration and drying of the formed crystals.

Ammonium niobium oxalate obtained in the production process above described is a white solid, with a monoclinic crystal structure, with a niobium content in the range from 5 to 30% by weight, which is stable in contact with air at room temperature, and it is not polymerized by aging, it is water soluble, with a solubility in the range from 60 to 160 grams of niobium per liter of water, at temperatures from 20 to 80°C. It can be used as a niobium precursor, appropriate for the synthesis of functionalized materials such as ceramic, optical lenses, catalysts, high purity niobium oxides, thin films and crystals, wherein the niobium is the main constituent or is added in the composition as promoter or dopant.

BRIEF DESCRIPTION OF THE DRAWINGS

In the attached drawings:

Figure 1 is a flowchart of the process of production of the ammonium niobium oxalate.

Figure 2 is the basic molecular structure of the anion niobium oxalate wherein the niobium atom is coordinated by 7 oxygen atoms and 2 oxalate groups .

Figure 3 is the solubility in water of the ammonium niobium oxalate as a function of the solution temperature.

Figure 4 is the Raman spectrum of an aqueous solution of the ammonium niobium oxalate as a function of the pH of the solution: (a) pH 0,2; (b) pH 1,0; (c) pH 2,0; (d) pH 3,0; (e) pH 4,0; and (f) pH 5,0.

DESCRIPTIONS OF THE PREFERRED EMBODIMENTS

The flowchart of the process of production of the ammonium niobium oxalate is shown in Figure 1. The production process comprises the combination of several unitary operations, of which the steps are: opening or digestion of a niobium precursor compound with oxalic acid and ammonium salt; dilution of the opening solution; cooling for crystallization and precipitation of the oxalic acid in excess; filtration for removal of the precipitated oxalic acid; recycling of the oxalic acid; evaporation of the filtrate until an optimal density of the solution is reached; addition of a new amount of an ammonium salt; cooling for crystallization and precipitation of the ammonium niobium oxalate; filtration for removal of the precipitated ammonium niobium oxalate; and final drying of the ammonium niobium oxalate.

The opening or digestion of a niobium precursor compound is effected in aqueous solution of oxalic acid and an ammonium salt, in a jacketed vitrified reactor maintained under intense stirring. Digestion can be accomplished at atmospheric pressure at temperatures varying from 75 to 120°C, preferably in the range from 90 to 110°C. Several compounds can be used as niobium precursors and among them niobium pentoxide, hydrated niobium oxides, potassium niobate, sodium niobate, fluoro potassium niobate, fluoro sodium niobate, niobium sulfate and niobium hydroxide, the hydrated niobium oxide with water contents varying from 5 to 70% by weight being preferred, even more preferably with water contents in the range from 15 to 60% by weight. The ammonium salt can be selected among ammonium oxalate, ammonium chloride, ammonium acetate, ammonium hydroxide and ammonium nitrate, ammonium oxalate being preferred. The mass ratios of oxalic acid and ammonium salt in relation to the niobium content in the niobium precursor compound vary from 1 to 12, preferably in the range from 1 to 5, for the oxalic acid:niobium ratio and from 0.3 to 2,0 for the ammonium salt:niobium ratio. In this process step, the digestion promotes the attack of the niobium precursor compound by the oxalic acid thus forming niobium oxalate anions in aqueous phase $\{[NbO(C_2O_4)_2(H_2O)_2]\}$, that are stabilized by the cation ammonium (NH4+) derived from the ammonium salt.

A crystalline solution is obtained in the reactor after the digestion and to which more deionized water is added for dilution of the solution and cooling thereof to temperatures lower than 50°C. The dilution aims at reducing the density of the opening solution, which was greater than 1300 g/l, to values between 1000 and 1300 g/l, preferably in the range from 1090 to 1170 g/l and more preferably between 1110 and 1170 g/l. It follows a further cooling to temperatures in the range from 4 to 25°C, preferably between 4 and 17°C, with ice water in the reactor jacket, so that crystallization and precipitation of the oxalic acid in excess occurs for a period from 3 to 16 hours. The solution is then filtered or decanted for the removal of the oxalic acid crystals. The excess oxalic acid withdrawn in this filtration or decantation step did not react with the niobium precursor compound and corresponds to between 30 to 70% of the initial mass content in the opening solution, this being then recycled in the preparation of the opening solution (see Figure 1).

In the reactor, the filtrate solution is then evaporated, by passing steam in the reactor jacket, at pressures that vary from the atmospheric pressure (760 mmHg) to absolute pressures, in the range from 20 to 250 mmHg, preferably in the range from 70 to 180 mmHg. The evaporation proceeds until the desired density of the solution is reached, it being undesirable, however, that crystallization and precipitation of solids occur in this step. Typical densities vary from 1000 to 1500 g/l, preferably in the range from 1150 to 1300 g/l. Once reached the desired density, the solution is cooled to a temperature lower than 50°C, more ammonium salt being then added. The addition of ammonium salt in this step has the purpose of reintroducing ammonium ions which have been lost in the evaporation process, thus facilitating the crystallization of the ammonium niobium oxalate, besides preventing the problem of the the olation of ammonium niobium oxalate, which by aging, can undergo polymerization resulting in a water insoluble product. The ammonium salt can be selected among ammonium oxalate, ammonium chloride, ammonium acetate, ammonium hydroxide and ammonium nitrate, ammonium oxalate being preferred. The solution is then finally cooled to a temperature in the range from 4 to 22°C, preferably between 5 and 17°C, by the passage of ice water in the reactor jacket, for crystallization and precipitation of the ammonium niobium oxalate. Then it follows filtration or decantation and subsequent drying of the crystals of the product of this invention. Drying of the crystals can be done using compressed air, ketones or alcohols. The final yield of the process is in the range from 90 to 98% in relation to the initial amount of niobium oxide.

The ammonium niobium oxalate obtained in the production process described above is a white solid, of monoclinic crystal structure, with niobium content in the range from 5 to 30% by weight, with good stability in ambient atmosphere and water soluble. Its crystal structure was determined by X-ray diffraction (XRD). The basic molecular structure is $NH_4[NbO(C_2O_4)_2(H_2O)_2].(H_2O)_n$, with the niobium atom coordinated by two bidentate oxalate groups, as shown in Figure 2. Two water molecules and one oxygen atom form a pentagonal bi-pyramidal structure with the terminal double bond Nb=O. Ammonium group (NH_4^+) is surrounded by seven oxygen atoms in an irregular arrangement, six oxygen atoms belonging to the oxalate groups and one to the niobyil radical.

The solubility of the produced ammonium niobium oxalate is a function of the temperature and can vary from 60 to 160 grams of niobium per liter of water at temperatures varying from 20 to 80°C, see Figure 3. The aqueous solutions of the ammonium niobium oxalate present turbidity numbers lower than 90 NTU. In order to increase the solubility of the ammonium niobium oxalate from 30 to 40% by weight, oxalic acid in a diluted aqueous solution is added where the concentrations do not exceed 0.2 M. In accordance with the Raman spectroscopy of figure 4, when the ammonium niobium oxalate is dissolved in water, ionic species of niobium oxide containing one, two or three oxalate groups are formed. Nevertheless, the chemical balance of these ionic species is a function of the pH of the solution (Fig. 4). In solutions with pH lower than 4.0, it is observed, by Raman, bands at 940-913 cm^{-1}, which are characteristic of the drawing mode of the Nb=O bond in which the Nb atom is coordinated with 3 or 2 oxalate groups. The bands at 580-560 cm^{-1} are related to the drawing mode of Nb-O-C bonds, while the drawing mode of the $Nb\text{-}OH_2$ bond appears in the region of 320-280 cm^{-1}. All these species are present in aqueous solutions of the ammonium niobium oxalate prepared in a pH range varying from 0.2 to 4. For values higher than 4, bands relating to hydrated Nb_2O_5, around 662 cm^{-1}, appear due to the polymerization process of the niobium oxalate ions which entails the precipitation thereof.

The ammonium niobium oxalate can be used as soluble niobium precursor for the preparation of functionalized materials in which niobium is a part of the composition. Stability in ambient atmosphere and water solubility render this compound a very attractive material alternative to the other niobium precursors such as pentachlorides, fluorides, niobates, alkoxides and even other oxalates, due to the necessity, for some of them, of being handled in controlled atmosphere without the presence of moisture, in addition to the fact that they do not possess the same water solubility. Another positive aspect of the ammonium niobium oxalate is that the calcination step for decomposition of the niobium precursor does not generate gases that are corrosive and noxious to the environment, minimizing the costs of equipments for scrubbing gases and controlling fumes. The decomposition is rather clean, releasing gases like O_2, CO_2, CO, H_2O, NO_x, H_2 and N_2.

The use of the ammonium niobium oxalate as a soluble niobium precursor is very broad, and it can have several applications in the production of functionalized materials such as ceramic, optical lenses, catalysts, high purity niobium oxides, thin films, crystals and the like where niobium is the main constituent or is used in promoting or doping the subject material. Any technique of preparation of materials that requires a soluble niobium precursor such as sol-gel, precipitation, impregnation, deposition, decomposition and hydro treatment and others can make use of a solution of the ammonium niobium oxalate.

Some typical examples of preparation and use of the ammonium niobium oxalate follow:

EXAMPLE 1:

In a vitrified reactor of 1000 ml, a solution containing 298 liters of deionized water and 320 kg of oxalic acid is prepared. The solution is heated to 90°C and under stirring 82 kg of ammonium oxalate and thereafter 190 kg of hydrated niobium oxide, as for instance, niobia HY® (35,8% by weight of Nb), produced and marketed by CBMM (Companhia Brasileira de Metalurgia e Mineração) are added. The system is kept heated and under stirring until the complete solubilization of all components. After total dissolution, 720 ml of deionized water are added. It follows then the cooling of the solution down to 12°C so that crystallization and precipitation of the oxalic acid in excess occur. After filtration, the filtrate is returned to the reactor where the solution is evaporated until reaching the density of 1300 g/l. It follows cooling of the solution down to 40°C and, under stirring, 12 kg of ammonium oxalate are added. The solution is kept under stirring for the complete dissolution of the ammonium oxalate. The solution is then cooled to a temperature of 10°C, so as to crystallize and precipitate the ammonium niobium oxalate. It follows lastly the filtration in press filters followed by drying of the end product with compressed air. Typical characteristics of the ammonium niobium oxalate produced through this process are:

- Niobium content: 10 to 30% by weight;
- Solubility in water: from 60 to 160 g Nb/l of water at temperatures from 20 to 80°;
-Turbidity: < 90 NTU;
- Monoclinic crystal structure.
- Molecular formula: $NH_4[NbO(C_2O_4)_2(H_2O)_2]. (H_2O)_n$

EXAMPLE 2:

This example deals with the use of the ammonium niobium oxalate for the production of a crystal grade niobium oxide.

In a reactor of 1500 ml a solution containing 300 kg of ammonium niobium oxalate (produced according to example 1) and 1000 l of deionized water is prepared. The solution is heated to 60°C and under stirring 200 l of ammonium hydroxide (25%) are added. The precipitated material, the crystal grade niobium oxide, is filtered for 3 times with 1000 l of deionized water heated to 90°C. Typical characteristics of the crystal grade niobium oxide produced through this process are:

% Nb_2O_5: 99.99

% TaO_5: 0.0025 - 0,1

% Fe: < 0.0003

% Na and K: < 0.0003

% Ti < 0.0003

% Si < 0.0003

% Ni, Cr, Co, Cu, Pb, Ca < 0.0001

% Al: < 0.0003.

CLAIMS

1. Process of production of ammonium niobium oxalate characterized in that the production process comprises the combination of several unitary operations, of which the steps are

a. digestion of a niobium precursor compound in an aqueous solution of oxalic acid and ammonium salt,

b. dilution of the opening solution;

c. cooling to the temperature necessary for the crystallization and precipitation of the oxalic acid in excess;

d. filtration or decantation of the solution for removal of the oxalic acid crystals;

e. recycling of the oxalic acid;

f. evaporation of the solution of the filtrate until an optimal density of solution is reached;

g. addition of a new amount of ammonium salt;

h. final cooling of the solution for crystallization and precipitation of the ammonium niobium oxalate; and

i. filtration and drying of the crystals of ammonium niobium oxalate.

2. Process in accordance with claim 1, characterized in that that the digestion is accomplished under atmospheric pressure.

3. Process in accordance with claim 1, characterized in that the digestion is accomplished at temperatures varying from 75 to 120°C.

4. Process in accordance with claim 1, characterized in that the digestion is accomplished at temperatures varying from 90 to 110°C.

5. Process in accordance with claim 1, characterized in that the niobium precursor compound used is selected among niobium pentoxide, hydrated niobium oxide, potassium niobate, calcium niobate, fluoro potassium niobate, fluoro sodium niobate, niobium sulfate and niobium hydroxide.

6. Process in accordance with claim 1, characterized in that the niobium precursor compound used is hydrated oxide niobium.

7. Process in accordance with claim 6, characterized in that the hydrated niobium oxide has water contents that vary from 5 to 70% by weight.

8. Process in accordance with claim 6, characterized in that the hydrated niobium oxide has water contents of water that vary from 15 to 60% by weight.

9. Process in accordance with claim 1, characterized in that the mass ratio between oxalic acid and niobium precursor compound is in the range from 1 to 12.

10. Process in accordance with claim 1, characterized in that the mass ratio between oxalic acid and niobium precursor compound is in the range from 1 to 5.

11. Process in accordance with claim 1, characterized in that the ammonium salt used is selected among ammonium oxalate, ammonium chloride, ammonium acetate, ammonium hydroxide and ammonium nitrate.

12. Process in accordance with claim 1, characterized in that the ammonium salt used is ammonium oxalate.

13. Process in accordance with claim 1, characterized in that the mass ratio between the ammonium salt and the niobium precursor compound is in the range from 0.3 to 2.0.

14. Process in accordance with claim 1, characterized in that the

opening solution is diluted so as to obtain a density in the range from 1000 to 1300 g/l.

15. Process in accordance with claim 14, characterized in that the density of the opening solution is in the range from 1090 to 1170 g/l.

16. Process in accordance with claim 14, characterized in the density of the opening solution is in the range from 1100 to 1170 g/l.

17. Process in accordance with claim 1, characterized in that the temperature of cooling of the solution for crystallization precipitation of the oxalic acid in excess is in the range from 4 to 25°C.

18. Process in accordance with claim 1, characterized in that the temperature of cooling of the solution for crystallization and precipitation of the oxalic acid in excess is in the range from 4 to 17°C.

19. Process in accordance with claim 1, characterized in that the yield of oxalic acid in excess withdrawn after filtration of the solution is in the range from 30 to 70% of the initial mass content added in the opening solution.

20. Process in accordance with claim 1, characterized in that the oxalic acid obtained after filtration or decantation is recycled.

21. Process in accordance with claim 1, characterized in that the evaporation of the filtrate is done at pressures that vary from the atmospheric pressure (760 mmHg) to absolute pressures in the range of 20 to 250 mmHg.

22. Process in accordance with claim 1, characterized in that the evaporation of the filtrate is done at pressures that vary from the atmospheric pressure (760 mmHg) to absolute pressures in the range of 70 to 180 mmHg.

23. Process in accordance with claim 1, characterized in that the optimal density to be reached during evaporation of the filtrate varies from 1000 to 1500 g/l.

24. Process in accordance with claim 1, characterized in that the optimal density to be reached during evaporation of the filtrate varies from 1150 to 1300 g/l.

25. Process in accordance with claim 1, characterized in that the new addition of the ammonium salt corresponds to a mass ratio between the ammonium salt and the niobium precursor compound in the range from 0.001 to 2.

26. Process in accordance with claim 25, characterized in that the ammonium salt used is selected among ammonium oxalate, ammonium, chloride, ammonium acetate, ammonium hydroxide and ammonium nitrate.

27. Process in accordance with claim 25, characterized in that the ammonium salt used is ammonium oxalate.

28. Process in accordance with claim 1, characterized in that the temperature of cooling of the solution for crystallization and precipitation of the ammonium niobium oxalate is in the range from 4 to 22°C.

29. Process in accordance with claim 1, characterized in that the temperature of cooling of the solution for crystallization and precipitation of the ammonium niobium oxalate is in the range from 5 to 17°C.

30. Process in accordance with claim 1, characterized in that the ammonium niobium oxalate is dried after filtration at room temperature with compressed air, ketones or alcohols.

31. Process in accordance with claim 1, characterized in that the yield of the process in relation to the initial content of niobium oxide is from 90 to 98%.

32. Ammonium niobium oxalate characterized in that it has a defined crystal structure, niobium contents in a narrow range and controlled, and

is stable in contact with air and soluble in water.

33. Ammonium niobium oxalate in accordance with claim 32, characterized in that the crystal structure is monoclinic.

34. Ammonium niobium oxalate in accordance with claim 32, characterized in that the niobium content is in the range from 5 to 30% by weight.

35. Ammonium niobium oxalate in accordance with claim 32, characterized in that the solubility in water is in the range from 60 to 160 grams of niobium per liter of water at temperatures from 20 to 80°C.

36. Use of ammonium niobium oxalate characterized in that it is as a niobium precursor suited to the synthesis of functionalized materials.

37. Use in accordance with claim 36, characterized in that the functionalized materials are ceramic, optical lenses, catalysts, special oxides, thin films, crystals and others where niobium is the main constituent or is used in the promotion or doping of the material.

38. Use in accordance with claim 36, characterized in that the techniques of synthesis of functionalized materials comprise sol-gel, precipitation, deposition, impregnation, decomposition and hydro treatment.

39. Use in accordance with claim 36, characterized in that it is in the production of niobium oxide crystal grade with high index of purity.

40. Use in accordance with claim 39, characterized in that the synthesis of the niobium oxide crystal grade is for precipitation with an aqueous solution of ammonium hydroxide or ammonium gas.

41. Use in accordance with claim 40, characterized in that the aqueous solution of ammonium hydroxide has a concentration of NH_3 in the range from 1 to 25% NH_3 by weight.

42. Use in accordance with claim 40, characterized in that the aqueous solution of ammonium hydroxide has a concentration of NH_3 in the range from 5 to 20% by weight.

43. Use in accordance with claim 39, characterized in that the crystal grade niobium oxide produced presents a purity in the range from 99.9999 to 99.99% of Nb_2O_5.

44. Use in accordance with claim 39, characterized in that the crystal grade niobium oxide produced presents as impurities Fe < 3 ppm; Na and K < 50 ppm; Al < 10 ppm; Ti < 50 ppm; Ta < 300 ppm; Si < 30 ppm; Ni, Cr, Co, Cu, Pb, Ca < 20 ppm.

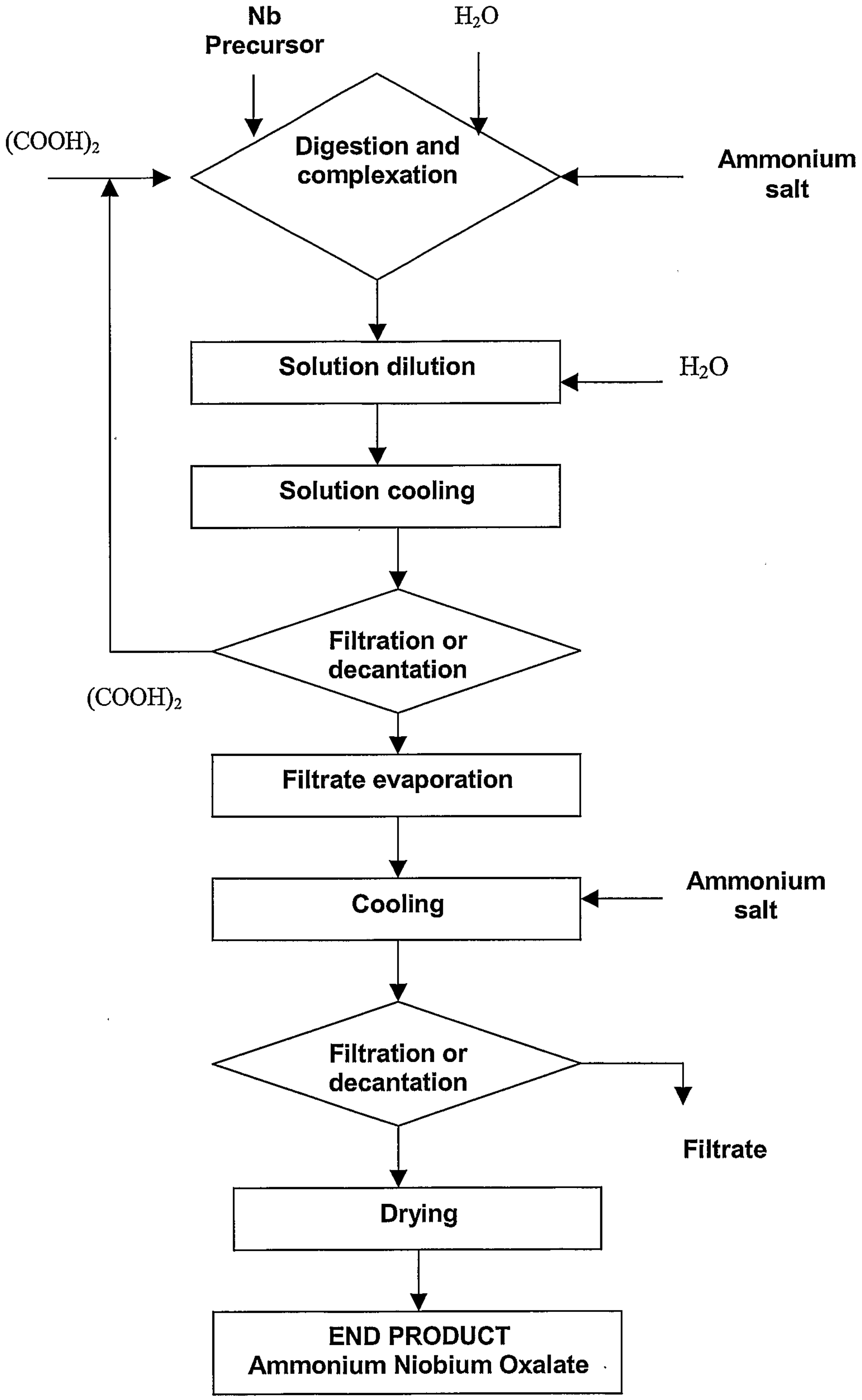
Nb
Precursor
H_2O
$(COOH)_2$
Digestion and complexation
Ammonium salt
Solution dilution
H_2O
Solution cooling
Filtration or decantation
$(COOH)_2$
Filtrate evaporation
Cooling
Ammonium salt
Filtration or decantation
Filtrate
Drying
END PRODUCT
Ammonium Niobium Oxalate

FIGURE 1

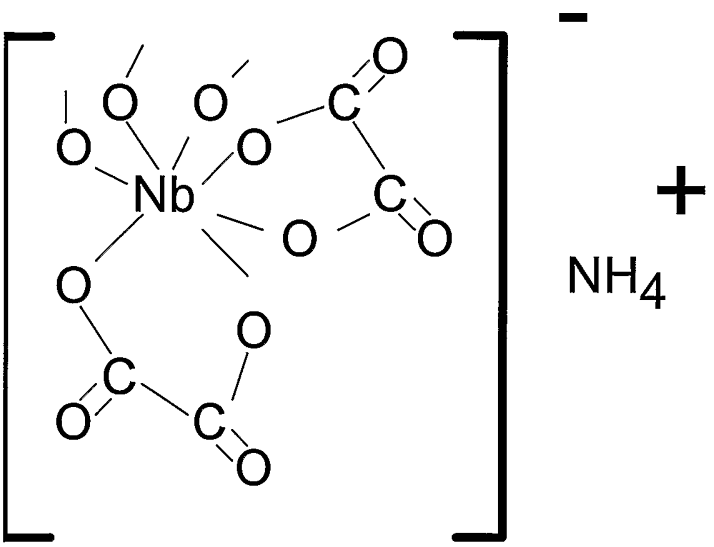

FIGURE 2

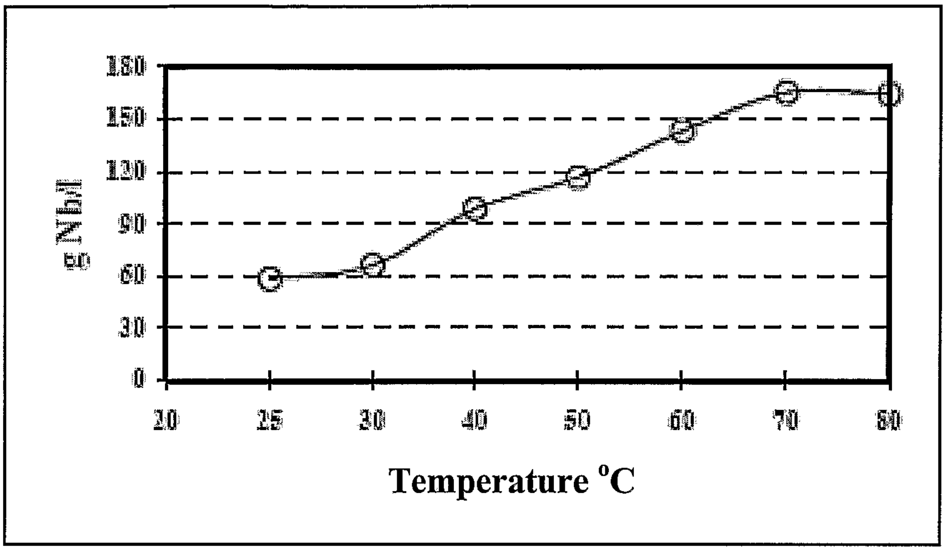

FIGURE 3

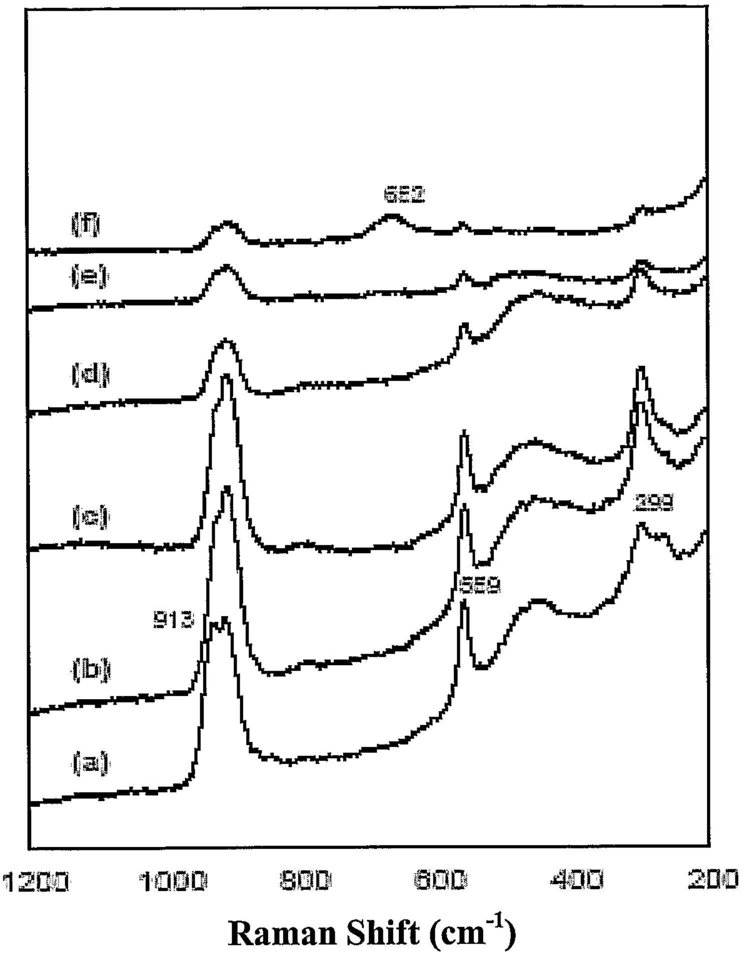
(f)
652
(e)
(d)
(c)
299
559
913
(b)
(a)
1200
1000
800
600
400
200
Raman Shift (cm-1)

FIGURE 4

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/BR2005/000186

A. CLASSIFICATION OF SUBJECT MATTER
C01G33/00

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)
C01G

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 409 391 A (MOSHEIM CHARLES E) 5 November 1968 (1968-11-05) the whole document	1-44
X	US 6 036 880 A (KOMADA ET AL) 14 March 2000 (2000-03-14) cited in the application	32,34-42
A	column 8, line 65 - column 16, line 40 examples 3,8	1-31
X	EP 0 603 836 A (MITSUBISHI KASEI CORPORATION; MITSUBISHI CHEMICAL CORPORATION) 29 June 1994 (1994-06-29) examples	32,34-38

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 23 November 2005	Date of mailing of the international search report 30/11/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Besana, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte[illegible]ional Application No
PCT/BR2005/000186

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3409391 A	05-11-1968	NONE	
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EP 0603836 A	29-06-1994	DE 69318684 D1	25-06-1998
		DE 69318684 T2	14-01-1999
		US 5422328 A	06-06-1995