Notice

DESCRIPTION CN118183830A

A calcium-doped barium titanate powder, its preparation method and application

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一种钙掺杂钛酸钡粉体及其制备方法和应用

[0001]

Technical Field

技术领域

[n0001]

This invention belongs to the field of nano-ceramic powder preparation, specifically referring to a calcium-doped barium titanate powder, its preparation method, and its application.

本发明属于纳米陶瓷粉体制备领域，特别是指一种钙掺杂钛酸钡粉体及其制备方法和应用。

[0003]

Background Technology

背景技术

[n0002]

Barium titanate is an important basic raw material for multilayer ceramic capacitors (MLCCs) due to its high dielectric properties, environmental friendliness, and non-toxicity. As MLCCs gradually develop towards miniaturization, large capacity, and high reliability, higher requirements are being placed on the particle size, dispersibility, tetragonal phase, and other structural parameters of barium titanate.

钛酸钡因具有高介电性能，且对环境友好、无毒性等特性是多层陶瓷电容器(MLCC)重要基础原材料，随着MLCC逐渐向小型化、大容量、高可靠性等方向发展，对钛酸钡的颗粒尺寸、分散性、四方相等结构参数提出来更高的要求。

[n0003]

Meanwhile, the dielectric constant of barium titanate ceramics varies greatly with temperature, and near the Curie temperature, the dielectric constant undergoes a sudden change, manifested as a very sharp Curie peak. Furthermore, its wide hysteresis loop and low breakdown strength limit its widespread application in energy storage capacitors.

同时钛酸钡陶瓷的介电常数随温度的变化很大，而且在居里温度附近，介电常数会发生突变，表现在居里峰非常尖锐，而且具有宽的电滞回线和低的击穿强度限制了其在储能电容器中的广泛应用。

Barium titanate is an ABO-NER1-perovskite structure, and its high-temperature stability can be improved by doping different metal elements into Ba or Ti sites in the crystal lattice.

钛酸钡是一种ABO₃钙钛矿结构，通过在晶格中掺杂不同的金属元素进入Ba位或者Ti位来提高其高温温度稳定性。

Appropriate calcium doping can shift the Curie temperature in BaTiO₃ towards higher temperatures, expand the temperature range of the tetragonal phase, broaden the Curie peak, and improve temperature stability.

适量的钙掺杂可以使得BaTiO₃中的居里温度向高温方向移动，四方相的温度区间扩大，居里峰变宽，温度稳定性更好。

The inclusion of calcium in the barium titanate lattice can not only effectively reduce the grain size and thus improve energy storage performance, but also enhance the stability of the ceramic under high pressure and reduce dielectric loss.

钙进入钛酸钡晶格中，不仅可以有效减小晶粒尺寸从而提升储能性能，而且还可以提高陶瓷在高压环境下的稳定性，同时还能降低介电损耗。

[n0004]

Currently, solid-phase and liquid-phase methods are commonly used to synthesize calcium-doped barium titanate powder. Solid-phase methods use abundant and readily available raw materials, have simple and convenient processes, low production costs, and mature technology. However, the synthesized powder has a large particle size, severe particle agglomeration, poor dispersibility, and the reaction needs to be carried out at high temperatures, which consumes a lot of energy.

目前合成钙掺杂钛酸钡粉体常用固相法和液相法，固相法原料丰富易得、工艺简单方便、生产成本低、技术成熟，但是合成的粉体粒径大、颗粒团聚严重、分散性差、并且反应需在高温下进行、耗能大。

Zhang Lei et al. synthesized calcium-doped barium titanate powder using a rotary kiln low-high speed two-stage calcination solid-state method. Compared with the traditional one-stage high-temperature solid-state calcination, the obtained calcium-doped barium titanate has the advantages of uniform particle size and high tetragonality, but the average particle size is 1.32 μm, which is relatively large.

张蕾等人采用回转炉低-高速两段煅烧固相法合成钙掺杂的钛酸钡粉体，相比于传统的一段高温固相煅烧，获得的钙掺杂钛酸钡具有粒径均匀、四方性较高等优点，但颗粒的平均尺寸在1.32um，颗粒尺寸较大。

Zhu Guisheng et al. synthesized calcium-doped barium titanate powder with an average particle size of about 100 nm and good dispersibility through a hydrothermal method. However, the reaction requires a high concentration of KOH as a mineralizing agent, and a large amount of water is needed to wash away the alkaline mineralizing agent. Moreover, it is easy to leave trace amounts of alkaline or alkaline earth metal ions in the barium titanate body, which makes it unsuitable for use in the field of high-purity electronic materials. This is because they used H₂TiO₃ as the titanium source, which contains a large number of hydroxyl groups in its structure. The calcium-doped barium titanate powder prepared by them has a high hydroxyl defect and a low tetragonal phase content (c/a = 1.0036), which cannot meet the requirements of practical applications.

朱归胜等人通过水热法，合成了平均粒径100nm左右的、分散性较好的钙掺杂钛酸钡粉体，但反应需要高浓度的KOH作为矿化剂辅助完成，后续需要大量的水洗来洗涤碱性矿化剂，而且容易造成微量的碱性或者碱土金属离子在钛酸钡本体中的残留而无法应用于高纯度电子材料领域，因为其采用H₂TiO₃为钛源，其结构中含有大量的羟基，其制备的钙掺杂钛酸钡粉体羟基缺陷较高，四方相含量较低(c/a＝1.0036)，无法满足实际应用需求。

[0007]

Summary of the Invention

发明内容

[n0005]

To address the technical problems of large particle size, wide distribution, poor dispersibility, high defect content, low tetragonal phase content, and large amount of mineralizer required in the solid-phase method of preparing barium titanate, this invention proposes a barium titanate powder, its preparation method, and its application. This invention produces small-sized, highly dispersed barium titanate powder with a high tetragonal phase content, and the preparation process is simple and does not require the addition of mineralizer.

为了解决现有技术中固相法制备的钙掺杂钛酸钡粒径尺寸较大、分布较宽、分散性差以及液相法缺陷含量高，四方相含量低以及需要大量的矿化剂的技术问题，本发明提出了一种钙掺杂钛酸钡粉体及其制备方法和应用，制备出小尺寸、高分散、四方相含量较高的的钙掺杂钛酸钡粉体，且制备过程中无需加入矿化剂、工艺简单。

[n0006]

To achieve the above objectives, the technical solution of the present invention is implemented as follows:

为实现上述目的，本发明的技术方案是这样实现的：

[n0007]

A method for preparing calcium-doped barium titanate powder, comprising the following steps:

一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0008]

(1) Prepare a barium salt solution of a certain concentration, heat to dissolve, and after complete dissolution, cool down and add an appropriate amount of calcium source.

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(1)配制一定浓度的钡盐溶液，加热溶解，溶解完全后降温后加入适量的钙源；

[n0009]

(2) Weigh the titanium source according to a certain barium-calcium molar ratio, add it to a barium salt solution containing calcium, and emulsify and shear at high speed to obtain a calcium-doped barium titanate precursor solution.

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(2)按照一定量的钡钙摩尔比称量钛源，加入到含有钙的钡盐溶液中，高速乳化剪切，得到钙掺杂钛酸钡前驱体溶液；

[n0010]

(3) The calcium-doped barium titanate precursor solution was transferred to a high-temperature reactor and hydrothermally reacted to obtain a barium titanate suspension.

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(3)将钙掺杂钛酸钡前驱体溶液转移至高温反应釜中，进行水热反应得到钛酸钡悬浮液；

[n0011]

(4) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

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(4)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤、干燥以及研磨后得到钙掺杂钛酸钡粉体。

[n0012]

In step (1), the barium source in the barium salt solution is Ba(OH)₂・8H₂O, the solvent is deionized water, and the concentration of the barium salt solution is 2-3 mol/L.

所述步骤(1)中钡盐溶液中钡源为Ba(OH)₂・8H₂O，溶剂为去离子水，钡盐溶液的浓度为2-3mol/L。

[n0013]

In step (1), the temperature for heating and dissolving the barium salt solution is 70-90°C, and after complete dissolution, the temperature is lowered to 40-50°C.

所述步骤(1)中加热溶解钡盐溶液的温度为70-90℃，待完全溶解后降温到40-50℃。

[n0014]

In step (1), the calcium source is one or a mixture of two or more of CaCl₂, Ca(NO₃)₂, Ca(CH₃COO)₂ and Ca(H₂PO₄)₂.

所述步骤(1)中钙源为CaCl₂、Ca(NO₃)₂、Ca(CH₃COO)₂和Ca(H₂PO₄)₂中的一种或两种以上的混合物。

[n0015]

In step (1), the molar ratio of calcium source to barium source is (1-10):(90-99).

所述步骤(1)中钙源和钡源的摩尔比为(1-10)：(90-99)。

[n0016]

In step (2), the titanium source is anatase titanium dioxide formed by treating titanate nanotubes (NTA) at 300-700℃ for 0.5-8h.

所述步骤(2)中钛源为钛酸纳米管(NTA)经过在300-700°C，处理0.5-8h后形成的锐钛矿二氧化钛。

[n0017]

In step (2), the molar ratio of (barium source + calcium source) / titanium source is (1.0-1.2):1.

所述步骤(2)中(钡源+钙源)/钛源的摩尔比为(1.0-1.2)：1。

[n0018]

The hydrothermal reaction in step (3) is carried out at a temperature of 160-200°C for 8-48 hours.

所述步骤(3)中水热反应的温度为160-200°C，时间为8-48h。

[n0019]

The calcium-doped barium titanate powder prepared by the above preparation method.

上述制备方法制备的钙掺杂钛酸钡粉体。

[n0020]

The above-mentioned calcium-doped barium titanate powder is used in multilayer ceramic capacitors.

上述钙掺杂钛酸钡粉体在多层陶瓷电容器中的应用。

[n0021]

The beneficial effects of this invention are:

本发明产生的有益效果是：

[n0022]

(1) In this invention, titanate nanotubes ($H_2Ti_2O_4(OH)_2$, NTA) have a one-dimensional tubular structure, which is converted into anatase titanium dioxide after high-temperature calcination.

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(1)本发明中钛酸纳米管($H_2Ti_2O_4(OH)_2$，NTA)具有一维管状结构，经过高温煅烧其转化为锐钛矿二氧化钛。

This titanium dioxide has the characteristics of small particle size and high dispersibility, and its structure has a high oxygen vacancy content, which affects the Ti-O bond length around the vacancy, changes the local coordination environment, and generates a reduction surface. All of these are conducive to improving the reactivity of titanium dioxide. This titanium dioxide also has the characteristics of uniform size distribution, which keeps the dissolution-nucleation rate relatively consistent.

该二氧化钛具有颗粒尺寸小，分散性较高等特点，且结构具有较高的氧空位含量，影响了空位周围的Ti—O键键长，改变局域配位环境，产生还原表面，这都有利于提高二氧化钛的反应活性，该二氧化钛还具有均匀的尺寸分布，使溶解-成核速率保持相对一致等特点。

When used as a titanium source for the hydrothermal preparation of calcium-doped barium titanate, it exhibits good reactivity, a mild and easily controllable reaction process, and the prepared calcium-doped barium titanate has the advantages of small particle size (average particle size ≤100nm), high dispersibility, uniform calcium distribution, and high tetragonal phase content.

当其用作水热法制备钙掺杂钛酸钡的钛源时，具有较好的反应活性，反应过程温和易于控制，制备得到的钙掺杂钛酸钡具有颗粒尺寸小(平均粒径约≤100nm)、分散性高、钙元素分布均匀、四方相含量高的优点。

[n0023]

(2) The present invention uses titanium dioxide after heat treatment of titanate nanotubes as titanium source. The high reactivity in the hydrothermal process avoids the use of high concentration of inorganic alkali mineralizer. This reduces the subsequent large amount of water washing process and avoids the residue of trace alkaline or alkaline earth metal ions in barium titanate body, thereby meeting the requirements of MLCC for the purity of raw materials.

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(2)本发明以钛酸纳米管经过热处理后的二氧化钛为钛源，在水热过程中较高的反应活性，避免了使用高浓度的无机碱矿化剂，这一方面减少了后续的大量的水洗过程，另外一方面避免了微量的碱性或者碱土金属离子在钛酸钡本体中的残留，从而满足MLCC对原材料纯度的要求。

[n0024]

(3) The preparation method proposed in this invention avoids the problems of high energy consumption and large particle size and serious particle agglomeration caused by the high-temperature calcination process of solid phase method, and also avoids the problem of using mineralizers in the traditional liquid phase preparation process. This method is low in cost, safe, simple in process, and can also realize the large-scale production of powder, which meets the development requirements of subsequent high-temperature, thin-layer and multilayer ceramic capacitor products.

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(3)本发明提出的制备方法既避免了固相法的高温煅烧过程引发能耗大以及其制备的粉体粒径尺寸大、颗粒团聚严重的问题，又避免了传统液相制备该过程中需要使用矿化剂的问题，该方法成本低、安全性好、工艺简单、亦可实现粉体的大规模生产，满足后续高温、薄层多层陶瓷电容器产品的开发要求。

[0028]

Attached Figure Description

附图说明

[n0025]

To more clearly illustrate the technical solutions in the embodiments of the present invention or the prior art, the drawings used in the description of the embodiments or the prior art will be briefly introduced below. Obviously, the drawings described below are only some embodiments of the present invention. For those skilled in the art, other drawings can be obtained based on these drawings without creative effort.

为了更清楚地说明本发明实施例或现有技术中的技术方案，下面将对实施例或现有技术描述中所需要使用的附图作简单地介绍，显而易见地，下面描述中的附图仅仅是本发明的一些实施例，对于本领域普通技术人员来讲，在不付出创造性劳动的前提下，还可以根据这些附图获得其他的附图。

[n0026]

Figure 1 shows the XRD pattern (a), SEM pattern (b), and ESR spectrum (c) of the titanium dioxide source used in Example 1 of this invention.

图1为本发明实施例1使用的二氧化钛钛源的XRD图(a)和SEM图(b)和ESR谱图(c)。

[n0027]

Figure 2 shows the SEM image (a), particle size distribution (b), and elemental distribution (c) of the calcium-doped barium titanate powder prepared in Example 1 of the present invention.

图2为本发明实施例1制备钙掺杂钛酸钡粉末的SEM图(a)、粒径分布图(b)及元素分布图(c)。

[n0028]

Figure 3 is a SEM image of calcium-doped barium titanate prepared using titanate nanotubes as the titanium source in Comparative Example 1 of this invention.

图3为本发明对比例1使用钛酸纳米管为钛源制备的钙掺杂钛酸钡的SEM图。

[n0029]

Figure 4 shows SEM images of the calcium-doped barium titanate powders prepared in Examples 2-4 of this invention, where (a) Example 2; (b) Example 3; and (c) Example 4.

图4为本发明实施例2-4制备的钙掺杂钛酸钡粉末的SEM图，其中，(a)实施例2；(b)实施例3；(c)实施例4。

[n0030]

Figure 5 shows the XRD patterns of the calcium-doped barium titanate powders prepared in Examples 1-4 of this invention.

图5为本发明实施例1-4制备的钙掺杂钛酸钡粉末的XRD图。

[n0031]

Figure 6 shows SEM images of calcium-doped barium titanate powders with different calcium contents prepared in this invention and their corresponding particle size distribution diagrams, wherein (a) Example 5; (b) Example 6; (c) Example 7; (d) Example 8; (c) Example 9.

图6为本发明制备的不同钙含量的钙掺杂钛酸钡粉末的SEM图及其对应的粒径分布图，其中，(a)实施例5；(b)实施例6；(c)实施例7；(d)实施例8；(c)实施例9。

[0036]

Detailed Implementation

具体实施方式

[n0032]

The technical solution of the present invention will be clearly and completely described below with reference to the embodiments of the present invention. Obviously, the described embodiments are only some embodiments of the present invention, and not all embodiments.

下面将结合本发明实施例，对本发明的技术方案进行清楚、完整地描述，显然，所描述的实施例仅仅是本发明一部分实施例，而不是全部的实施例。

Based on the embodiments of this invention, all other embodiments obtained by those skilled in the art without creative effort are within the scope of protection of this invention.

基于本发明中的实施例，本领域普通技术人员在没有付出创造性劳动前提下所获得的所有其他实施例，都属于本发明保护的范围。

[n0033]

The preparation method of titanate nanotubes used in this invention is as follows: TiO20TiO21O2H2O is dispersed in 80 mL of 10 M NaOH solution, stirred evenly, and then placed in a polytetrafluoroethylene hydrothermal reactor and reacted at 120 °C for 24 h to prepare Na2OTiO22H2O. Then, Na2OTiO25OH26H27O is washed with water until pH = 10, then acid-washed with HCl solution at pH = 1.0 until pH = 1.2, stirred for 4-5 h, washed again with water to remove Cl28O until neutral, filtered, and finally dried in a vacuum oven at 60 °C. The obtained product is titanate nanotube (H29TiO30OH31H22O), abbreviated as NTA.

本发明中使用的钛酸纳米管的制备方式如下：将TiO₂分散在80mL，10M NaOH溶液中，搅拌均匀后置于聚四氟乙烯水热反应釜中，并在120℃反应24h，即可制备Na₂Ti₂O₅・H₂O，随后将Na₂Ti₂O₅・H₂O水洗至pH＝10，再用pH＝1.0的HCl溶液酸洗至pH＝1.2，搅拌4-5h，再次水洗去除Cl⁻至中性，抽滤，最后置于60℃真空烘箱干燥，所得产品即为钛酸纳米管(H₂Ti₂O₅・H₂O)，简称NTA。

[n0034]

Example 1

实施例1

[n0035]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0036]

(1) A certain amount of titanate nanotubes were weighed and placed in a muffle furnace and heat-treated at 600°C for 2 hours to obtain anatase titanium dioxide.

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(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0037]

(2) Weigh high-purity Ba(OH)33・8H34O, add deionized water to prepare 2.5M Ba(OH) 35・8H36O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH3COO)38O, controlling the molar ratio of barium source to calcium source to be 95:5.

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(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85℃待完全溶解后，自然降温至45℃后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为95：5。

[n0038]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

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(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0039]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

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(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0040]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

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(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0041]

Figure 1 is a structural characterization diagram of the titanium dioxide source used in this embodiment.

图1为本实施例所使用的二氧化钛钛源的结构表征图。

As can be seen from the XRD pattern in Figure 1a, the titanium dioxide source has an anatase crystal structure. As can be seen from the SEM pattern in Figure 1b, the titanium dioxide particles are composed of small particles of 20-50 nm with uniform dispersion. As can be seen from Figure 1c, its structure is rich in bound single-electron oxygen vacancies, which are all conducive to improving its reactivity.

从图1a XRD图可以看出该二氧化钛钛源为锐钛矿晶型结构，图1b SEM图可以看出，该二氧化钛颗粒是有20-50nm的小颗粒组成，颗粒分散均匀，从图1c可以看出其结构中富含束缚单电子氧空位，这些都有利于提高其反应活性。

[n0042]

Figure 2 shows the SEM image, particle size distribution, and elemental distribution of the calcium-doped barium titanate powder prepared in this embodiment.

图2为本实施例制备的钙掺杂钛酸钡粉末的SEM图、粒径分布图以及元素分布图。

Figures 2a and 2b are SEM images and particle size distribution diagrams of the prepared powder, respectively. It can be seen that the average particle size of the calcium-doped barium titanate powder prepared under this preparation process is about 97 nm. The particle size is uniform, the distribution is narrow, and the dispersibility is good.

图2a和图2b分别为制备粉体的SEM图和粒径分布图，可以看出，该制备工艺条件下制备得到的钙掺杂钛酸钡粉体平均粒径约为97nm，粒径大小均匀，分布较窄，分散性好。

Figure 2c shows the elemental distribution of calcium-doped barium titanate powder. It can be seen from the figure that calcium is uniformly distributed inside the barium titanate.

图2c为钙掺杂钛酸钡粉末的元素分布图，从图中可以看出钙元素在钛酸钡内部中均匀分布。

[n0043]

Example 2

实施例2

[n0044]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0045]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 300°C for 2 hours to obtain anatase titanium dioxide.

----

(1)称取一定量钛酸纳米管放置于马弗炉中，在300°C下热处理2h得到锐钛矿二氧化钛。

[n0046]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为95：5。

[n0047]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0048]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0049]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0050]

Example 3

实施例3

[n0051]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0052]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 400°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在400°C下热处理2h得到锐钛矿二氧化钛。

[n0053]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为95：5。

[n0054]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0055]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0056]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0057]

Example 4

实施例4

[n0058]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0059]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 700°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在700°C下热处理2h得到锐钛矿二氧化钛。

[n0060]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为95：5。

[n0061]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt, and control the molar ratio of (Ba

source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0062]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0063]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0064]

Example 5

实施例5

[n0065]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0066]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0067]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 99:1.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为99：1。

[n0068]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O and Ca(CH₃COO)₂ solution, and control the molar ratio of (Ba source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源到配制好的Ba(OH)₂・8H₂O和Ca(CH₃COO)₂溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0069]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 220°C for 24 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在220℃下水热反应24h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0070]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0071]

Example 6

实施例6

[n0072]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0073]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0074]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 98:2.

---

(2)称量高纯度Ba(OH)₂·8H₂O，加入去离子水配制2.5M的Ba(OH)₂·8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为98：2。

[n0075]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂·8H₂O and Ca(CH₃COO)₂ solution, and control the ratio of (Ba source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源到配制好的Ba(OH)₂·8H₂O和Ca(CH₃COO)₂溶液，(Ba源+Ca源)/Ti源的尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0076]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 220°C for 24 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在220°C下水热反应24h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0077]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0078]

Example 7

实施例7

[n0079]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0080]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0081]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 97:3.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为97：3。

[n0082]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O and Ca(CH₃COO)₂ solution, and control

the molar ratio of (Ba source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源到配制好的Ba(OH)₂・8H₂O和Ca(CH₃COO)₂溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0083]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 220°C for 24 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在220°C下水热反应24h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0084]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0085]

Example 8

实施例8

[n0086]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0087]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0088]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 96:4.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为96：4。

[n0089]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O and Ca(CH₃COO)₂ solution, and control the molar ratio of (Ba source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源到配制好的Ba(OH)₂・8H₂O和Ca(CH₃COO)₂溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0090]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 220°C for 24 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在220°C下水热反应24h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0091]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0092]

Example 9

实施例9

[n0093]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0094]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0095]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 90:10.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为90：10。

[n0096]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O and Ca(CH₃COO)₂ solution, and control the molar ratio of (Ba source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源到配制好的Ba(OH)₂・8H₂O和Ca(CH₃COO)₂溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0097]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 220°C for 24 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在220°C下水热反应24h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0098]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0099]

Example 10

实施例10

[n0100]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0101]

(1) A certain amount of titanate nanotubes were weighed and placed in a muffle furnace and heat-treated at 600°C for 0.5h to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理0.5h得到锐钛矿二氧化钛。

[n0102]

(2) Weigh high-purity Ba(OH)・8HO, add deionized water to prepare 2M Ba(OH)・8HO, stir and heat to 70°C until completely dissolved, then let it cool naturally to 40°C and add CaCl, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2M的Ba(OH)₂・8H₂O搅拌加热到70°C待完全溶解后，自然降温至40°C后加入CaCl₂，控制钡源和钙源的摩尔比为95：5。

[n0103]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0104]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0105]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0106]

Example 11

实施例11

[n0107]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0108]

(1) A certain amount of titanate nanotubes were weighed and placed in a muffle furnace and heat-treated at 300°C for 8 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在300°C下热处理8h得到锐钛矿二氧化钛。

[n0109]

(2) Weigh high-purity Ba(OH)・8HO, add deionized water to prepare 3M Ba(OH)・8HO, stir and heat to 90°C until completely dissolved, then let it cool naturally to 50°C and add Ca(NO), controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制3M的Ba(OH)₂・8H₂O搅拌加热到90°C待完全溶解后，自然降温至50°C后加入Ca(NO₃)₂，控制钡源和钙源的摩尔比为95：5。

[n0110]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1.2:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.2：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0111]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0112]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0113]

Example 12

实施例12

[n0114]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0115]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0116]

(2) Weigh high-purity Ba(OH)・8HO, add deionized water to prepare 2M Ba(OH)・8HO, stir and heat to 70°C until completely dissolved, then let it cool naturally to 40°C and add CaCl, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2M的Ba(OH)₂・8H₂O搅拌加热到70°C待完全溶解后，自然降温至40°C后加入CaCl₂，控制钡源和钙源的摩尔比为95：5。

[n0117]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1.1:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.1：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0118]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 220°C for 8 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在220°C下水热反应8h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0119]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0120]

Example 13

实施例13

[n0121]

The preparation method of calcium-doped barium titanate powder in this embodiment includes the following steps:

本实施例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0122]

(1) Weigh a certain amount of titanate nanotubes and place them in a muffle furnace. Heat treat them at 600°C for 2 hours to obtain anatase titanium dioxide.

---

(1)称取一定量钛酸纳米管放置于马弗炉中，在600°C下热处理2h得到锐钛矿二氧化钛。

[n0123]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2M Ba(OH)₂・8H₂O, stir and heat to 70°C until completely dissolved, then let it cool naturally to 40°C and add CaCl₂, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2M的Ba(OH)₂・8H₂O搅拌加热到70°C待完全溶解后，自然降温至40°C后加入CaCl₂，控制钡源和钙源的摩尔比为95：5。

[n0124]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O solution containing calcium salt. The molar ratio of (Ba source + Ca source)/Ti source is controlled at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源加入到配制好的含有钙盐的Ba(OH)₂・8H₂O溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0125]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 160°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在160°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0126]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0127]

Comparative Example 1

对比例1

[n0128]

The preparation method of calcium-doped barium titanate powder in this comparative example includes the following steps:

本对比例的一种钙掺杂钛酸钡粉体的制备方法，步骤如下：

[n0129]

(1) Titanate nanotubes that have not undergone temperature treatment were used as the titanium source.

---

(1)以没有经过温度处理的钛酸纳米管为钛源。

[n0130]

(2) Weigh high-purity Ba(OH)₂・8H₂O, add deionized water to prepare 2.5M Ba(OH)₂・8H₂O, stir and heat to 85°C until completely dissolved, then let it cool naturally to 45°C and add Ca(CH₃COO)₂, controlling the molar ratio of barium source to calcium source to be 95:5.

---

(2)称量高纯度Ba(OH)₂・8H₂O，加入去离子水配制2.5M的Ba(OH)₂・8H₂O搅拌加热到85°C待完全溶解后，自然降温至45°C后加入Ca(CH₃COO)₂，控制钡源和钙源的摩尔比为95：5。

[n0131]

(3) Add the titanium source prepared in step (1) to the prepared Ba(OH)₂・8H₂O and Ca(CH₃COO)₂ solution, and control the molar ratio of (Ba source + Ca source)/Ti source at 1.06:1. Shear at 1000 rpm for 3 min to obtain calcium-doped barium titanate precursor solution.

---

(3)加入步骤(1)中制备的钛源到配制好的Ba(OH)₂・8H₂O和Ca(CH₃COO)₂溶液，(Ba源+Ca源)/Ti源的摩尔比控制在1.06：1，1000rmp下高速剪切3min，得到钙掺杂钛酸钡前驱体溶液。

[n0132]

(4) The calcium-doped barium titanate precursor solution was transferred to a high-pressure reactor and hydrothermally reacted at 200°C for 48 hours. After cooling to room temperature, a calcium-doped barium titanate suspension was obtained.

---

(4)将钙掺杂钛酸钡前驱体溶液转移到高压反应釜中，在200°C下水热反应48h后，冷却至室温，得到钙掺杂钛酸钡悬浮液。

[n0133]

(5) The calcium-doped barium titanate suspension was filtered, washed with deionized water, dried and ground to obtain calcium-doped barium titanate powder.

---

(5)将钙掺杂钛酸钡悬浮液进行抽滤、去离子水洗涤，烘干、研磨后得到钙掺杂钛酸钡粉体。

[n0134]

Figure 3 shows the calcium-doped barium titanate powder prepared in this comparative example. As can be seen from the figure, the calcium-doped barium titanate particles prepared using NTA as the titanium source have not grown completely and the particle size agglomeration is quite serious.

图3为本对比例制备的钙掺杂钛酸钡粉体，从图中可以看出，以NTA为钛源制备得到的钙掺杂钛酸钡的颗粒生长不太完整，颗粒尺寸团聚比较严重。

[n0135]

Test case

测试例

[n0136]

The prepared barium titanate powder was subjected to performance tests. The grain size was observed using a scanning electron microscope (SEM). The tetragonality c/a of the powder was obtained by XRD testing and refinement.

对制备出的钛酸钡粉体进行性能测试，利用扫描电镜(SEM)观察晶粒大小；利用XRD测试并精修得到粉体四方性c/a。

The synthesized powder was characterized using a nanoparticle size and zeta potential analyzer, and the non-uniformity coefficient MD = (D₉₀-D₁₀) /D₅₀ was obtained. The smaller the MD, the more uniform the sample.

采用纳米粒度及zeta电位分析仪对合成的粉体进行表征，可以得到不均匀系数MD＝(D₉₀-D₁₀)/D₅₀，MD越小表示样品越均匀。

The effects of heat treatment of titanate nanotubes and calcium content on the properties of calcium-doped barium titanate powder were investigated.

分别探究了钛酸纳米管热处理和钙含量对钙掺杂钛酸钡粉体性能的影响。

[n0137]

(1) The effects of different heat treatments on the properties of calcium-doped barium titanate powder are shown in Figure 4, Figure 5 and Table 1.

---

(1)钛酸纳米管的不同热处理对钙掺杂钛酸钡粉体性能的影响，结果如图4、图5和表1所示。

[n0138]

Figure 4 shows scanning electron microscope images of the calcium-doped barium titanate powders prepared in Examples 2-4. As can be seen from the figure, the average particle sizes of the prepared calcium-doped barium titanate powders at heat treatment temperatures of 300°C, 400°C and 700°C are 95nm, 100nm and 88nm, respectively. The particle sizes are uniform, the distribution is narrow, and the dispersibility is good.

图4为实施例2-4制备的钙掺杂钛酸钡粉体的扫描电镜图，从图中可以看出，在热处理温度为300°C、400°C以及700°C时，制备的钙掺杂钛酸钡粉体平均粒径分别为95nm、100nm、88nm，且粒径大小均匀，分布较窄，分散性好。

[n0139]

Figure 5 shows the XRD patterns of the calcium-doped barium titanate powders prepared in Examples 1-4. As can be seen from the figure, the characteristic peaks of pure barium titanate are obtained, and no impurity peaks appear, which indicates that calcium has entered the barium titanate lattice to form a solid solution.

图5为实施例1-4制备的钙掺杂钛酸钡粉体的XRD图谱，从图中可以看出，得到为纯相的钛酸钡特征峰，无杂峰出现，即说明钙已进入钛酸钡晶格中形成固溶体。

[n0140]

Table 1. Effect of different heat-treated titanium sources on the properties of calcium-doped barium titanate powder

---

表1不同热处理钛源对钙掺杂钛酸钡粉体性能的影响

[n0142]

As can be seen from Table 1, the calcium-doped barium titanate prepared from titanium dioxide obtained by calcining NTA at 600°C for 2 hours has a high tetragonal phase content and a low non-uniformity coefficient. Therefore, 600°C is the optimal calcination temperature.

从表1中可以看出，NTA经过600°C，2h的煅烧处理得到的二氧化钛为钛源制备的钙掺杂钛酸钡具有高的四方相含量，同时其不均匀系数较低，因此600°C处理是较佳的煅烧温度。

[n0143]

(2) The effect of different barium source/calcium source molar ratios on the properties of calcium-doped barium titanate powder is shown in Figure 6 and Table 2.

---

(2)不同钡源/钙源的摩尔比对钙掺杂钛酸钡粉体性能的影响，结果如图6和表2所示。

[n0144]

Figure 6 shows scanning electron microscope images of the calcium-doped barium titanate powders prepared in Examples 5-9 and their corresponding particle size distributions. As can be seen from the figure, the synthesized powder particles are small in size and have a relatively uniform particle size distribution.

图6为实施例5-9制备的钙掺杂钛酸钡粉体的扫描电镜图及其相对应的粒径分布，从图中可以看出，合成的粉体颗粒尺寸较小，且粒径分布较为均匀。

[n0145]

Table 2. Effect of barium source/calcium source molar ratio on the properties of calcium-doped barium titanate powder

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表2钡源/钙源的摩尔比对钙掺杂钛酸钡粉体性能的影响

[n0146]

Examples of Barium Source/Calcium Source Molar Ratio (c/a) MD Example 1 95:5 1.0074 0.723 Example 5 99:1 1.0073 0.931 Example 6 98:2 1.0072 1.156 Example 7 97:3 1.0069 0.732 Example 8 96:4 1.0070 0.979 Example 9 90:10 1.0072 0.986

实施例 钡源/钙源的摩尔比 c/a MD 实施例1 95：5 1.0074 0.723 实施例5 99：1 1.0073 0.931 实施例6 98：2 1.0072 1.156 实施例7 97：3 1.0069 0.732 实施例8 96：4 1.0070 0.979 实施例9 90：10 1.0072 0.986

[n0147]

As can be seen from Table 2, when the molar ratio of barium source to calcium source is 95:5, it exhibits a higher tetragonal phase content and a lower inhomogeneity coefficient.

从表2中可以看出，钡源/钙源的摩尔比为95：5时，表现出较高的四方相含量和较低的不均匀系数。

[n0148]

In summary, this invention proposes a method for preparing calcium-doped barium titanate powder without the need for mineralizers. When using titanium dioxide obtained by high-temperature calcination of titanate nanotubes as the titanium source for preparing calcium-doped barium titanate by hydrothermal method, the titanium dioxide has small particle size, high dispersibility and high oxygen vacancy content, thus successfully preparing calcium-doped barium titanate powder with small particle size, uniform size, narrow distribution, good dispersibility and high tetragonal phase content.

综上所述，本发明提出了一种无需矿化剂的，钙掺杂钛酸钡粉体的制备方法，以钛酸纳米管经过高温煅烧后的二氧化钛作水热法制备钙掺杂钛酸钡的钛源时，由于该二氧化钛具有颗粒尺寸小，分散性较高且结构具有较高的氧空位含量，成功制备了粒径小，尺寸均匀，分布较窄，分散性好且出四方相含量较高的钙掺杂钛酸钡粉体。

This invention avoids the use of high-concentration inorganic alkali mineralizers, thus avoiding extensive water washing processes and the residue of alkaline ions in calcium-doped barium titanate powder, and meeting the high purity requirements of powder materials for electronic components.

本发明避免使用高浓度的无机碱矿化剂，可以避免大量的水洗过程以及碱性离子在钙掺杂钛酸钡粉体中的残留，满足电子元器件对粉体材料高纯度的要求。

[n0149]

The above description is only a preferred embodiment of the present invention and is not intended to limit the present invention. Any modifications, equivalent substitutions, improvements, etc., made within the spirit and principles of the present invention should be included within the protection scope of the present invention.

以上所述仅为本发明的较佳实施例而已，并不用以限制本发明，凡在本发明的精神和原则之内，所作的任何修改、等同替换、改进等，均应包含在本发明的保护范围之内。