Notice

DESCRIPTION CN116534893A

A solid-phase synthesis method for calcium-doped barium titanate powder

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一种钙掺杂钛酸钡粉体的固相合成法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of ceramic powder preparation technology, and in particular to a solid-phase synthesis method for calcium-doped barium titanate powder.

本发明涉及陶瓷粉体制备技术领域，尤其涉及一种钙掺杂钛酸钡粉体的固相合成法。

[0003]

Background Technology

背景技术

[n0002]

$BaTiO_3$ is a ferroelectric perovskite with a high room temperature dielectric constant of 2000-3000 and a moderate Curie temperature (T_C) of 120°C.

$BaTiO_3$是一种铁电钙钛矿，具有较高的室温介电常数2000-3000和适中的居里温度(T_C)120°C。

Currently, BaTiO3-based ceramics form the cornerstone of X7R multilayer ceramic capacitors.

目前，BaTiO₃基陶瓷构成了X7R多层陶瓷电容器的基石。

However, in order to meet the X8R specification, the operating range of the device needs to be extended to 150°C.

然而，为了满足X8R规格，器件的工作范围需要扩展到150°C。

In the prior art, T_C can be improved through appropriate chemical doping. Although it is known that A-site dopants such as Pb²⁺ and Bi³⁺ can achieve this effect, this method is subject to environmental regulations and/or is not suitable for processing in the reducing atmosphere required to manufacture the base electrode. Ca²⁺, Ba₁₋_xCa_xTiO₃ prepared as A-site dopant, with appropriate addition of T_C.

现有技术中，通过适当的化学掺杂可以提高T_C。 虽然已知A位掺杂剂如Pb²⁺和Bi³⁺可以实现该效果，但该种手段受到环境法规的制约，并且/或不适合在制造母材电极所需的还原气氛下进行加工。 Ca²⁺，作为A位点掺杂剂制备的Ba₁₋_xCa_xTiO₃，适度增加T_C。

[n0003]

The preparation methods of barium titanate are mainly divided into two categories: solid-phase method and liquid-phase method.

钛酸钡的制备方法主要分为两大类：固相法和液相法。

Powders prepared by liquid phase method have fine and uniform grains, but the cost is high and the process is complicated. In addition, during the preparation of liquid phase method such as hydrothermal reaction, there are a large number of hydroxyl and proton defects in the crystal lattice. During the calcination process, a large number of point defects will aggregate to form pores, which will reduce the powder density and suppress tetragonal distortion. Therefore, it is not suitable for use in high-reliability miniaturized MLCC devices. Solid-phase methods, such as planetary ball milling, are a traditional method for powder preparation. They use grinding media to mix and grind raw materials, and are characterized by low cost, high output and simple process. However, the resulting particles are often large and unevenly distributed. Therefore, choosing a suitable preparation method is of great importance for synthesizing barium calcium titanate powder with high c/a and small particle size.

液相法制备的粉体晶粒细小均匀，但是成本较高、工艺流程复杂，并且液相法如水热反应制备过程中晶格存在大量羟基、质子缺陷，煅烧过程中大量的点缺陷会聚集形成孔洞，降低粉体密度并抑制四方性畸变，不适合用于高可靠的小型化MLCC器件。 固相法，如行星球磨，是一种传统的粉体制备方

法，通过研磨介质将原料混匀、磨细，具有成本低、产量大、工艺简单的特点，但是往往得到的颗粒较大、分布不均匀。 因此选择合适的制备方法对于合成高c/a、小粒径的钛酸钡钙粉体具有重要作用。

[0006]

Summary of the Invention

发明内容

[n0004]

To address the aforementioned technical problems, this invention provides a solid-phase synthesis method for calcium-doped barium titanate powder.

针对上述技术问题，本发明提供一种钙掺杂钛酸钡粉体的固相合成法。

[n0005]

On the one hand, the present invention provides a solid-phase synthesis method for calcium-doped barium titanate powder, wherein the chemical composition of the calcium-doped barium titanate powder is (Ba_{1-x}Ca_x)_mTiO₃, wherein 0.00＜x＜0.08, 0.90＜m≤1;

一方面，本发明提供一种钙掺杂钛酸钡粉体的固相合成法，所述钙掺杂钛酸钡粉体的化学组成为(Ba_{1-x}Ca_x)_mTiO₃，其中，0.00＜x＜0.08，0.90＜m≤1；

[n0006]

The solid-phase synthesis method includes the following steps:

所述固相合成法包括以下步骤：

[n0007]

(1) Add titanium source, barium source and calcium source to solvent according to stoichiometric ratio to prepare mixed slurry and then grind it;

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(1)按照化学计量比将钛源、钡源和钙源加入溶剂配制成混合浆料然后进行研磨；

[n0008]

(2) Dry the slurry after grinding in step (1);

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(2)将步骤(1)经过研磨后的浆料进行烘干；

[n0009]

(3) The dried slurry from step (2) is crushed and sieved to obtain powder;

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(3)将步骤(2)烘干后的浆料进行粉碎过筛得到粉末；

[n0010]

(4) Heat the powder obtained in step (3) to 800-1000°C and keep it at that temperature for 1-5 hours.

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(4)将步骤(3)得到的粉末升温至800～1000°C保温1～5h。

[n0011]

In a preferred embodiment, in step (1), the titanium source is titanium dioxide;

作为优选地实施方式，步骤(1)中，所述钛源为二氧化钛；

[n0012]

Preferably, the barium source is barium carbonate;

优选地，所述钡源为碳酸钡；

[n0013]

Preferably, the calcium source is calcium carbonate;

优选地，所述钙源为碳酸钙；

[n0014]

Preferably, the solvent is ethanol.

优选地，所述溶剂为乙醇。

[n0015]

In a preferred embodiment, in step (1), the particle size of the titanium dioxide is 1 to 300 nm;

作为优选地实施方式，步骤(1)中，所述二氧化钛的粒径为1～300nm；

[n0016]

Preferably, the titanium dioxide has anatase crystal form;

优选地，所述二氧化钛的晶型为锐钛矿；

[n0017]

Preferably, the barium carbonate has a particle size of 1–100 nm;

优选地，所述碳酸钡的粒径为1～100nm；

[n0018]

Preferably, the calcium carbonate has a particle size of 1–200 nm.

优选地，所述碳酸钙的粒径为1～200nm。

[n0019]

In a preferred embodiment, the grinding in step (1) is sand grinding;

作为优选地实施方式，步骤(1)中，所述研磨为砂磨；

[n0020]

Preferably, the diameter of the abrasive media used in the abrasive mill is no greater than 0.1 mm;

优选地，所述砂磨采用的砂磨介质的直径不大于0.1mm；

[n0021]

Preferably, the milling speed is 1000-3000 r/min, and the milling time is 1-4 h;

优选地，所述砂磨的转速为1000～3000r/min，所述砂磨的时间为1～4h；

[n0022]

In some specific embodiments, the filling amount of the grinding media (i.e., the volume ratio of the grinding media to the grinding tank cavity) is 20-60%.

在某些具体的实施方式中，所述砂磨介质的填充量(即砂磨介质占砂磨罐腔体的体积比)为20～60%。

[n0023]

In a preferred embodiment, in step (2), the drying process is carried out at 80-100°C for 24-48 hours.

作为优选地实施方式，步骤(2)中，所述烘干为80～100°C烘干24～48h。

[n0024]

In a preferred embodiment, in step (3), the sieving is performed through a 100-300 mesh sieve.

作为优选地实施方式，步骤(3)中，所述过筛为过100～300目筛。

[n0025]

In a preferred embodiment, in step (4), the heating rate is 5 to 15 °C/min.

作为优选地实施方式，步骤(4)中，所述升温的速率为5～15°C/min。

[n0026]

In some specific embodiments, step (4) is followed by a grinding operation, wherein the grinding is performed to grind particles to a size of 200-300 nm.

在某些具体的实施方式中，步骤(4)后还包括研磨操作，所述研磨为研磨粒径至200～300nm。

[n0027]

In another aspect, the present invention provides calcium-doped barium titanate powder obtained by the above-described solid-phase synthesis method.

又一方面，本发明提供上述固相合成法得到的钙掺杂钛酸钡粉体。

[n0028]

In another aspect, the present invention provides the use of the above-mentioned calcium-doped barium titanate powder as a dielectric material.

又一方面，本发明提供上述钙掺杂钛酸钡粉体作为介电材料的用途。

[n0029]

Preferably, the calcium-doped barium titanate powder is used to prepare electronic components; more preferably, the electronic components are multilayer ceramic capacitors.

优选地，钙掺杂钛酸钡粉体用于制备电子元器件的用途，更优选地，电子元器件为多层陶瓷电容器。

[n0030]

The above technical solution has the following advantages or beneficial effects: The present invention uses a solid-state method to synthesize calcium-doped barium titanate powder. The prepared nano-calcium-doped barium titanate powder has excellent performance, high tetragonality, good crystallinity, small particle size, uniform particle size distribution, and smooth particle surface.

上述技术方案具有如下优点或者有益效果：本发明采用固相法合成钙掺杂钛酸钡粉体，制备得到的纳米钙掺杂钛酸钡粉体性能优异、四方性高、结晶度好、粒径小、粒径分布均匀，且颗粒表面光滑。

This method has a simple preparation process, is easy to operate, and has low raw material costs, making it suitable for large-scale industrialization.

该方法制备工艺简单，操作容易，原料成本低，适合大规模产业化。

The process provided by this invention fully demonstrates the advantages of solid-state methods in industrial preparation of small-particle-size, highly tetragonal powders, and is simple to operate, making it suitable for the preparation of multilayer ceramic capacitors (MLCCs).

本发明提供的工艺充分体现了固相法在工业上制备小粒径、高四方性粉体操作简单的优势，适用于制备多层陶瓷电容器(MLCC)。

[0034]

Attached Figure Description

附图说明

[n0031]

Figure 1 is a process flow diagram of the solid-phase synthesis method for preparing calcium-doped barium titanate powder in the embodiments and comparative examples of the present invention.

图1是本发明实施例以及对比例中固相合成法制备钙掺杂钛酸钡粉体的工艺流程图；

[n0032]

Figure 2 is a SEM image of the calcium-doped barium titanate powder prepared in Example 1 of the present invention;

图2是本发明实施例1所制备的钙掺杂钛酸钡粉体的SEM图；

[n0033]

Figure 3 is a SEM image of the calcium-doped barium titanate powder prepared in Example 2 of the present invention;

图3是本发明实施例2所制备的钙掺杂钛酸钡粉体的SEM图；

[n0034]

Figure 4 is a SEM image of the calcium-doped barium titanate powder prepared in Example 3 of the present invention;

图4是本发明实施例3所制备的钙掺杂钛酸钡粉体的SEM图；

[n0035]

Figure 5 is a SEM image of the calcium-doped barium titanate powder prepared in Comparative Example 1 of the present invention.

图5是本发明对比例1所制备的钙掺杂钛酸钡粉体的SEM图；

[n0036]

Figure 6 is a SEM image of the calcium-doped barium titanate powder prepared in Comparative Example 2 of the present invention.

图6是本发明对比例2所制备的钙掺杂钛酸钡粉体的SEM图；

[n0037]

Figure 7 is an XRD pattern of the calcium-doped barium titanate powder prepared in the embodiments and comparative examples of the present invention.

图7是本发明实施例以及对比例中所制备的钙掺杂钛酸钡粉体的的XRD图。

[0042]

Detailed Implementation

具体实施方式

[n0038]

The following embodiments are only some embodiments of the present invention, and not all embodiments.

下述实施例仅仅是本发明的一部分实施例，而不是全部的实施例。

Therefore, the detailed description of the embodiments of the present invention provided below is not intended to limit the scope of the claimed invention, but merely to illustrate selected embodiments of the invention.

因此，以下提供的本发明实施例中的详细描述并非旨在限制要求保护的本发明的范围，而是仅仅表示本发明的选定实施例。

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

基于本发明的实施例，本领域技术人员在没有作出创造性劳动的前提下所获得的所有其他实施例，都属于本发明的保护范围。

[n0039]

In this invention, unless otherwise specified, all equipment and raw materials can be purchased from the market or are commonly used in this industry.

在本发明中，若非特指，所有的设备和原料等均可从市场购得或是本行业常用的。

Unless otherwise specified, the methods described in the following embodiments are conventional methods in the art.

下述实施例中的方法，如无特别说明，均为本领域的常规方法。

[n0040]

Example 1

实施例1

[n0041]

As shown in Figure 1, in this embodiment, the solid-state synthesis of nano-calcium-doped barium titanate powder includes the following steps:

如图1所示，本实施例中，固相法合成纳米钙掺杂钛酸钡粉体包括以下步骤：

[n0042]

(1) Ingredients: Barium carbonate, titanium dioxide and calcium carbonate are mixed according to the stoichiometric ratio (Ba_{0.96}Ca_{0.04})_{0.95}TiO₃, and ethanol is added. After mixing, a powder slurry with a solid content of 30% is obtained.

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(1)配料：碳酸钡、二氧化钛、碳酸钙按照化学计量比(Ba_{0.96}Ca_{0.04})_{0.95}TiO₃配料，并加入乙醇，混合后得到固含量为30%的粉体浆料；

[n0043]

(2) Sand milling: The slurry obtained in step (1) is sand milled using zircon balls with a diameter of 0.1 mm as the sand milling medium, and the zircon ball filling amount is 40% (i.e., the sand milling medium accounts for the volume ratio of the sand milling tank cavity); the sand milling parameters are set as follows: sand milling speed 2000 r/min, sand milling time 2 h;

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(2)砂磨：将步骤(1)得到的浆料进行砂磨，采用直径为0.1mm的锆球为砂磨介质，锆球填充量40%(即砂磨介质占砂磨罐腔体的体积比)；砂磨的参数设置为：砂磨机转速2000r/min，砂磨时间为2h；

[n0044]

(3) Drying: Dry the slurry after sand milling at 90°C for 24 hours in an electric heating forced-air drying oven;

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(3)烘干：将砂磨后的浆料在电热鼓风干燥箱中90°C烘干24h；

[n0045]

(4) Sieving: The dried slurry is ground and pulverized in a mortar and passed through a 200-mesh sieve to obtain uniform powder;

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(4)过筛：烘干后的浆料用研钵研磨粉碎，过200目筛，得到均匀粉末；

[n0046]

(5) Calcination: Heat to 950°C at a rate of 10°C/min and hold for 1 hour;

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(5)煅烧：以10°C/min的速率升温至950°C，保温1h；

[n0047]

(6) Grinding: Grind the calcined product with a mortar and pestle to obtain barium calcium titanate powder.

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(6)研磨：将煅烧后的产物用研钵研磨，得到钛酸钡钙粉体。

[n0048]

The scanning electron microscope (SEM) image and particle size distribution map of the calcium-doped barium titanate powder prepared in this embodiment are shown in Figure 2. The average particle size of the sample is about 228 nm, the particle size distribution is uniform, and there are no abnormally large particles.

本实施例制备的钙掺杂钛酸钡粉体的扫描电子显微镜(SEM)图和粒径分布图如图2所示，样品的平均粒径约为228nm，粒径分布均匀，无异常大颗粒。

The X-ray diffraction (XRD) pattern is shown in Figure 7. There are no other impurities. There is a distinct splitting peak at the characteristic peak $2\theta = 44\text{-}46°$, which corresponds to the (002) and (200) crystal planes of the tetragonal phase barium calcium titanate, respectively. The tetragonality $c/a = 1.0094$.

X射线衍射(XRD)图谱如图7所示，无其他杂相，在特征峰2θ＝44-46°处有明显的分裂峰，其分别对应于四方相钛酸钡钙的(002)和(200)的晶面，四方性c/a＝1.0094。

[n0049]

Example 2

实施例2

[n0050]

As shown in Figure 1, in this embodiment, the solid-state synthesis of nano-calcium-doped barium titanate powder includes the following steps:

如图1所示，本实施例中，固相法合成纳米钙掺杂钛酸钡粉体包括以下步骤：

[n0051]

(1) Ingredients: Barium carbonate, titanium dioxide and calcium carbonate are mixed according to the stoichiometric ratio (Ba_{0.99}Ca_{0.01})_{0.95}TiO₃, and ethanol is added. After mixing, a powder slurry with a solid content of 30% is obtained.

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(1)配料：碳酸钡、二氧化钛、碳酸钙按照化学计量比(Ba_{0.99}Ca_{0.01})_{0.95}TiO₃配料，并加入乙醇，混合后得到固含量为30%的粉体浆料；

[n0052]

(2) Sand milling: The slurry obtained in step (1) is sand milled using zirconium balls with a diameter of 0.1 mm as the sand milling medium, and the zirconium ball filling amount is 40%; the sand milling parameters are set as follows: sand mill speed 2000 r/min, sand milling time 2 h;

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(2)砂磨：将步骤(1)得到的浆料进行砂磨，采用直径为0.1mm的锆球为砂磨介质，锆球填充量40%；砂磨的参数设置为：砂磨机转速2000r/min，砂磨时间为2h；

[n0053]

(3) Drying: Dry the slurry after sand milling at 90°C for 24 hours in an electric heating forced-air drying oven;

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(3)烘干：将砂磨后的浆料在电热鼓风干燥箱中90°C烘干24h；

[n0054]

(4) Sieving: The dried slurry is ground and pulverized in a mortar and passed through a 200-mesh sieve to obtain uniform powder;

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(4)过筛：烘干后的浆料用研钵研磨粉碎，过200目筛，得到均匀粉末；

[n0055]

(5) Calcination: Heat to 950°C at a rate of 10°C/min and hold for 1 hour;

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(5)煅烧：以10°C/min的速率升温至950°C，保温1h；

[n0056]

(6) Grinding: Grind the calcined product with a mortar and pestle to obtain barium calcium titanate powder.

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(6)研磨：将煅烧后的产物用研钵研磨，得到钛酸钡钙粉体。

[n0057]

The scanning electron microscope (SEM) image and particle size distribution map of the calcium-doped barium titanate powder prepared in this embodiment are shown in Figure 3.

The average particle size of the sample is about 219 nm, the particle size distribution is uniform, and there are no abnormally large particles.

本实施例制备的钙掺杂钛酸钡粉体的扫描电子显微镜(SEM)图和粒径分布图如图3所示，样品的平均粒径约为219nm，粒径分布均匀，无异常大颗粒。

The X-ray diffraction (XRD) pattern is shown in Figure 7. There are no other impurities. There is a distinct splitting peak at the characteristic peak 2θ = 44-46°, which corresponds to the (002) and (200) crystal planes of the tetragonal phase barium calcium titanate, respectively. The tetragonality c/a = 1.0087.

X射线衍射(XRD)图谱如图7所示，无其他杂相，在特征峰2θ＝44-46°处有明显的分裂峰，其分别对应于四方相钛酸钡钙的(002)和(200)的晶面，四方性c/a＝1.0087。

[n0058]

Example 3

实施例3

[n0059]

As shown in Figure 1, in this embodiment, the solid-state synthesis of nano-calcium-doped barium titanate powder includes the following steps:

如图1所示，本实施例中，固相法合成纳米钙掺杂钛酸钡粉体包括以下步骤：

[n0060]

(1) Ingredients: Barium carbonate, titanium dioxide and calcium carbonate are mixed according to the stoichiometric ratio (Ba_{0.93}Ca_{0.07})_{0.95}TiO₃, and ethanol is added. After mixing, a powder slurry with a solid content of 30% is obtained.

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(1)配料：碳酸钡、二氧化钛、碳酸钙按照化学计量比(Ba_{0.93}Ca_{0.07})_{0.95}TiO₃配料，并加入乙醇，混合后得到固含量为30%的粉体浆料；

[n0061]

(2) Sand milling: The slurry obtained in step (1) is sand milled using zirconium balls with a diameter of 0.1 mm as the sand milling medium, and the zirconium ball filling amount is 40%; the sand milling parameters are set as follows: sand mill speed 2000 r/min, sand milling time 2 h;

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(2)砂磨：将步骤(1)得到的浆料进行砂磨，采用直径为0.1mm的锆球为砂磨介质，锆球填充量40%；砂磨的参数设置为：砂磨机转速2000r/min，砂磨时间为2h；

[n0062]

(3) Drying: Dry the slurry after sand milling at 90°C for 24 hours in an electric heating forced-air drying oven;

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(3)烘干：将砂磨后的浆料在电热鼓风干燥箱中90°C烘干24h；

[n0063]

(4) Sieving: The dried slurry is ground and pulverized in a mortar and passed through a 200-mesh sieve to obtain uniform powder;

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(4)过筛：烘干后的浆料用研钵研磨粉碎，过200目筛，得到均匀粉末；

[n0064]

(5) Calcination: Heat to 950°C at a rate of 10°C/min and hold for 1 hour;

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(5)煅烧：以10°C/min的速率升温至950°C，保温1h；

[n0065]

(6) Grinding: Grind the calcined product with a mortar and pestle to obtain barium calcium titanate powder.

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(6)研磨：将煅烧后的产物用研钵研磨，得到钛酸钡钙粉体。

[n0066]

The scanning electron microscope (SEM) image and particle size distribution map of the calcium-doped barium titanate powder prepared in this embodiment are shown in Figure 4. The average particle size of the sample is about 213 nm, the particle size distribution is uniform, and there are no abnormally large particles.

本实施例制备的钙掺杂钛酸钡粉体的扫描电子显微镜(SEM)图和粒径分布图如图4所示，样品的平均粒径约为213nm，粒径分布均匀，无异常大颗粒。

The X-ray diffraction (XRD) pattern is shown in Figure 7. There are no other impurities. There is a distinct splitting peak at the characteristic peak 2θ = 44-46°, which corresponds to the (002) and (200) crystal planes of the tetragonal phase barium calcium titanate, respectively. The tetragonality c/a = 1.0081.

X射线衍射(XRD)图谱如图7所示，无其他杂相，在特征峰2θ＝44-46°处有明显的分裂峰，其分别对应于四方相钛酸钡钙的(002)和(200)的晶面，四方性c/a＝1.0081。

[n0067]

Comparative Example 1

对比例1

[n0068]

This comparative example uses the same method as Example 1, except that the stoichiometric ratio of the calcium-doped barium titanate powder is (Ba_{0.96}Ca_{0.04})_{1.05}TiO₃.

本对比例采用与实施例1相同的方法，区别仅在于，钙掺杂钛酸钡粉体的化学计量比为(Ba_{0.96}Ca_{0.04})_{1.05}TiO₃。

The XRD of the calcium-doped barium titanate powder obtained in this comparative example is shown in Figure 7. The characteristic peak at 2θ = 44-46° is a single peak, with no obvious splitting peak. The synthesized barium calcium titanate powder is mainly cubic phase.

本对比例得到的钙掺杂钛酸钡粉体的XRD如图7所示，在特征峰2θ＝44-46°处为单峰，无明显劈裂峰，合成的钛酸钡钙粉体为主要是立方相晶型。

The SEM image of the calcium-doped barium titanate powder obtained in this comparative example is shown in Figure 5. The particle size of the calcium-doped barium titanate powder is relatively large. This is because when the molar ratio of (Ba+Ca) to Ti is greater than 1, Ca²⁺ can be forced to occupy Ti sites, and the resulting oxygen vacancies promote particle growth.

本对比例得到的钙掺杂钛酸钡粉体的的SEM图如图5所示，钙掺杂钛酸钡粉体的粒径尺寸偏大，原因是当(Ba+Ca)与Ti的摩尔比大于1时，可迫使Ca²⁺占据Ti位，产生的氧空位促进了颗粒的生长。

[n0069]

Comparative Example 2

对比例2

[n0070]

This comparative example uses the same method as Example 1, except that the stoichiometric ratio of the calcium-doped barium titanate powder is (Ba_{0.96}Ca_{0.04})_{0.90}TiO₃.

本对比例采用与实施例1相同的方法，区别仅在于钙掺杂钛酸钡粉体的化学计量比为(Ba_{0.96}Ca_{0.04})_{0.90}TiO₃。

The XRD pattern of the calcium-doped barium titanate powder obtained in this comparative example is shown in Figure 7. The characteristic peak at 2θ = 44-46° is a single peak with no obvious splitting peak. The synthesized calcium-doped barium titanate powder is mainly cubic phase.

本对比例得到的钙掺杂钛酸钡粉体的XRD图如图7所示，在特征峰2θ＝44-46°处为单峰，无明显劈裂峰，合成的钙掺杂钛酸钡粉体为主要是立方相晶型。

The SEM image of the calcium-doped barium titanate powder obtained in this comparative example is shown in Figure 6. The particle size of the calcium-doped barium titanate powder is relatively small because TiO₂ excessively inhibits the particle growth of (Ba_{0.96}Ca_{0.04})_{0.90}TiO₃.

本对比例得到的钙掺杂钛酸钡粉体的SEM图如图6所示，钙掺杂钛酸钡粉体的粒径尺寸偏小，原因是TiO₂过量抑制了(Ba_{0.96}Ca_{0.04})_{0.90}TiO₃的颗粒生长。

[n0071]

In summary, this invention synthesizes tetragonal phase nano-doped barium titanate powder using a solid-state method, producing highly tetragonal, uniformly sized barium titanate powder with an average particle size of approximately 250 nm. This provides a new approach for producing small-particle-size, highly tetragonal barium titanate powder.

综上所述，本发明采用固相法合成四方相纳米钙掺杂钛酸钡粉体，制备出高四方性、颗粒均匀，平均粒径约为250nm的钙掺杂钛酸钡粉体，为生产小粒径、高四方性的钙掺杂钛酸钡粉体提供新思路。

[n0072]

The above description is only a preferred embodiment of the present invention. It should be noted that for those skilled in the art, several improvements and modifications can be made without departing from the principle of the present invention, and these improvements and modifications should also be considered within the scope of protection of the present invention.

以上所述仅是本发明的优选实施方式，应当指出：对于本技术领域的普通技术人员来说，在不脱离本发明原理的前提下，还可以做出若干改进和润饰，这些改进和润饰也应视为本发明的保护范围。