Notice

DESCRIPTION CN113353973A

A method for preparing calcium-doped barium titanate powder

一种钙掺杂钛酸钡粉体的制备方法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of ceramic powder preparation technology, and in particular to a method for preparing calcium-doped barium titanate powder for multilayer ceramic capacitors (MLCCs).

本发明涉及陶瓷粉体制备技术领域，尤其涉及一种多层陶瓷电容器(Multi-layerCeramic Capacitors，以下简称MLCC)用的钙掺杂钛酸钡粉体的制备方法。

[0003]

Background Technology

背景技术

[n0002]

Barium titanate ceramics, as a ferroelectric material, have wide applications in the electronics industry, especially in the field of ceramic capacitors, where multilayer ceramic capacitors made of barium titanate account for the majority of the market share.

钛酸钡陶瓷作为一种铁电材料在电子工业领域有广泛的应用，尤其是在陶瓷电容领域，占市场主要份额的就是以钛酸钡为材料的多层陶瓷电容器。

The first step in preparing high-performance BaTiO_NER1-based ceramics is to synthesize high-purity, small-particle-size, highly tetragonal, and uniform-morphology high-performance BaTiO_NER2- powder.

制备高性能BaTiO₃基陶瓷的第一步是合成纯度高、粒度小、四方性高、形貌均匀的高性能BaTiO₃粉体。

[n0003]

The traditional methods for preparing BaTiO3 powder in industry are liquid phase method and solid phase method.

工业上制备BaTiO₃粉体的传统方法是液相法和固相法。

On the one hand, the liquid phase method is more expensive, and on the other hand, the solution ions form a crystal lattice from scratch, which inevitably introduces more lattice defects, making the liquid phase method less practical than the solid phase method.

液相法一方面成本较高，另一方面溶液离子从零组建晶格，不可避免地会引入较多晶格缺陷，使得液相法的实用性不如固相法高。

[n0004]

The solid-state method involves calcining a mixture of BaCO₃ and TiO₂ at high temperature to produce BaTiO₃ through a solid-state reaction.

固相法即将BaCO₃和TiO₂的混合物在高温下煅烧，发生固相反应获得BaTiO₃。

Traditional solid-state reactions require reaction temperatures above 1000°C. However, by reducing the particle size of the raw materials, using mechanical ball milling for activation, and increasing the contact area through uniform mixing, the required reaction temperature can be effectively reduced.

传统固相法需要1000°C以上的反应温度，通过降低原料粒度、使用机械球磨活化、均匀混合增加接触面积等，可以有效降低反应的所需温度。

During the preparation process, as the reaction temperature increases, the raw materials will undergo two stages of reaction. Generally, the reaction BaCO₃(S)+TiO₂(S)→BaTiO₃(S)+CO₂(g) occurs above 650°C (above 550°C for ball-milled activated powder).

制备过程中，随着反应温度的升高，原料将发生两个阶段的反应，一般在650°C以上(球磨活化的粉体在550°C以上)发生BaCO₃(S)+TiO₂(S)→BaTiO₃(S)+CO₂(g)的反应。

At temperatures above 820°C, the reactions BaCO₃(S)→BaO(S)+CO₂(g) and BaO(S)+TiO₂(S)→BaTiO₃(S) occur. Traditional solid-phase methods produce products with problems such as coarse particles and uneven particle size. Particle size is usually positively correlated with tetragonality, making it difficult to obtain high tetragonality while ensuring small particle size.

在820°C以上，发生BaCO₃(S)→BaO(S)+CO₂(g)和BaO(S)+TiO₂(S)→BaTiO₃(S)的反应。 传统固相法的产品存在着颗粒较粗、颗粒不均匀等问题，粒径通常与四方性存在正相关，因此难以在保证小粒径的同时获得高四方性。

[n0005]

In industry, the commonly used continuous high-temperature reactors are generally tunnel kilns or rotary kilns.

工业上常用的连续式高温反应炉一般为隧道窑或回转窑。

Compared to the static contact state of materials in tunnel kilns, the materials in rotary kilns undergo step-like movements, repeatedly going through the process of single-layer formation and collapse. The materials are constantly subjected to mixing disturbances, resulting in particles being in dynamic contact, which helps increase the contact opportunities between particles and makes the materials more uniformly mixed.

相比隧道窑中物料处于静态接触的状态，回转窑中的物料作阶梯运动，重复着单层区形成-崩落的过程，物料不停受到混合扰动，其结果是颗粒处于动态接触状态，有利于增加颗粒间的接触机会，使物料混合均匀。

[0008]

Summary of the Invention

发明内容

[n0006]

To address the aforementioned technical problems, this invention provides a method for solid-phase synthesis of calcium-doped barium titanate powder using a rotary furnace with

two rotation speeds (low and high). This method involves adjusting the furnace rotation speed during calcination to prepare calcium-doped barium titanate powder with uniform particle size and high tetragonality.

针对上述技术问题，本发明提供一种回转炉低-高两段转速固相合成钙掺杂钛酸钡粉体的方法，通过在煅烧中途调整炉腔转速来制备粒径均匀、高四方性的钙掺杂的钛酸钡粉体。

[n0007]

To achieve the above objectives, the technical solution adopted by the present invention is as follows:

为实现上述目的，本发明采取的技术方案为：

[n0008]

The first aspect of this invention provides a method for preparing calcium-doped barium titanate powder, comprising the following steps:

本发明第一方面提供一种钙掺杂钛酸钡粉体的制备方法，包括如下步骤：

[n0009]

Step (1): Mix titanium dioxide, barium carbonate and calcium carbonate evenly to obtain powder I; In the technical solution of the present invention, the barium source can also be other oxides or salts of barium, and the titanium source can also be other oxides or salts of titanium.

步骤(1)：将二氧化钛、碳酸钡、碳酸钙混合均匀后得到粉体I；在本发明的技术方案中，钡源也可以选用钡的其它氧化物或盐类，钛源也可以选用钛的其它氧化物、或盐类。

[n0010]

Step (2): Powder I is put into a rotary furnace for calcination at a temperature of 900-1000°C, a heating rate of 5-10°C/min, a furnace rotation speed of r₁, and a holding time of 1-2h.

步骤(2)：将粉体I投入回转炉中进行煅烧，煅烧温度为900～1000°C，升温速率为5到10°C/min，炉腔旋转速度为r₁，保温时间为1～2h；

[n0011]

Step (3): Adjust the furnace rotation speed to r₂, keep the calcination temperature constant, and continue to keep warm for 1-2 hours;

步骤(3)：调整炉腔旋转速度为r₂，保持煅烧温度不变，继续保温1～2h；

[n0012]

Step (4): Stop the heat preservation and cool to obtain calcium-doped barium titanate powder;

步骤(4)：停止保温，冷却即可得到钙掺杂钛酸钡粉体；

[n0013]

In step (2), the furnace rotation speed r₁ is less than the furnace rotation speed r₂ in step (3).

其中，步骤(2)中炉腔旋转速度r₁小于步骤(3)中炉腔旋转速度r₂。

[n0014]

Furthermore, in step (2), the furnace rotation speed r₁ is 1 to 4 rpm.

进一步地，步骤(2)中炉腔旋转速度r₁为1～4rpm。

[n0015]

Furthermore, in step (3), the furnace rotation speed r₂ is 8 to 10 rpm.

进一步地，步骤(3)中炉腔旋转速度r₂为8～10rpm。

[n0016]

Furthermore, in step (1), the molar ratio of titanium dioxide, barium carbonate, and calcium carbonate is 1:0.7-0.9:0.1-0.3.

进一步地，步骤(1)中，二氧化钛、碳酸钡、碳酸钙的摩尔比为1：0.7～0.9：0.1～0.3。

[n0017]

Furthermore, an air atmosphere is used inside the rotary kiln chamber.

进一步地，回转炉腔内使用空气气氛。

[n0018]

Furthermore, in step (4), the rotation speed of the furnace cavity during the cooling process remains unchanged from the rotation speed in step (3), and the cooling rate is 5 to 10 °C/min.

进一步地，步骤(4)中，冷却过程炉腔旋转速度保持步骤(3)中的旋转速度不变，降温速率为5～10℃/min。

[n0019]

A second aspect of the present invention provides a calcium-doped barium titanate powder prepared by the above-described preparation method.

本发明第二方面提供一种由上述制备方法制备的钙掺杂钛酸钡粉体。

[n0020]

A third aspect of the present invention provides the use of the above-mentioned calcium-doped barium titanate powder as a dielectric material, and further, its use in the preparation of multilayer ceramic capacitors.

本发明第三方面提供上述钙掺杂钛酸钡粉体作为介电材料的用途，进一步地，用于制备多层陶瓷电容器的用途。

[n0021]

This invention takes into account the different stages of powder calcination and utilizes the particle separation-contact dynamic process caused by the rotational motion of the rotary furnace. By adjusting the rotation speed at different stages of powder calcination, the separation-contact frequency of particles is adjusted. In the solid-phase reaction stage, an appropriate rotation speed is used to ensure uniform mixing of dissimilar particles and facilitate the reaction. In the grain growth stage, a higher rotation speed is used to frequently break the neck contact between particles, inhibiting the mass transfer growth of particles. This achieves high-temperature long-term heat preservation to improve the tetragonality of the product while inhibiting particle size growth, thereby preparing calcium-doped barium titanate powder with high tetragonality and uniform particle size.

本发明考虑到粉体煅烧经历的不同阶段，利用回转炉的回转运动造成的颗粒分离-接触动态过程，在粉体煅烧的不同阶段中通过调整转速来调整颗粒的分离-接触频率，在固相反应阶段用适当转速保证异种颗粒混合均匀，使反应顺利进行，在晶粒生长阶段使用较高转速，频繁打破颗粒间的颈部接触，抑制颗粒的传质生长，做到高温长时间保温提升产物四方性的同时，抑制粒度增长，从而制备了高四方性、粒度均匀的钙掺杂的钛酸钡粉体。

[n0022]

The above technical solution has the following advantages or beneficial effects: The technical solution of the present invention is to prepare calcium-doped barium titanate powder by

using an improved solid-phase synthesis method. Through a two-stage calcination method of low-speed and high-speed rotary furnace, at low speed, the reactants titanium dioxide, barium carbonate, and calcium carbonate are kept in appropriate contact to complete the metathesis reaction to generate Ba_{1-x}Ca_xTiO₃. The heat preservation stage at high speed will play a role in lattice correction and improve tetragonality, while the particle size does not increase significantly.

上述技术方案具有如下优点或者有益效果：本发明的技术方案在于采用改进的固相合成法制备钙掺杂钛酸钡粉体，通过回转炉低-高速两段式煅烧法，低转速时，反应物二氧化钛、碳酸钡、碳酸钙保持适当接触，完成复分解反应生成Ba_{1-x}Ca_xTiO₃，高转速下的保温阶段将对其起到晶格修正，提高四方性的作用，同时粒度无明显的增长。

[n0023]

Compared to traditional muffle furnace solid-phase synthesis, the calcium-doped barium titanate powder produced by the method provided in this invention has the characteristics of uniform particle size and high tetragonality, and can be used to prepare multilayer ceramic capacitors.

相对于传统的马弗炉固相合成，本发明提供的方法制造的钙掺杂的钛酸钡粉体，具有粒径均匀、四方性高的特点，可用于制备多层陶瓷电容器。

[n0024]

This invention can obtain the corresponding final stoichiometric product by changing the optimal ratio of raw materials titanium dioxide, barium carbonate, and calcium carbonate, and can control the particle properties of the product by changing the process.

本发明可以通过改变原料二氧化钛、碳酸钡、碳酸钙的最佳配比得到相应的最终化学计量产物，并且可通过改变工艺过程控制产品的颗粒性质。

[0028]

Attached Figure Description

附图说明

[n0025]

Figure 1 is a schematic diagram of the temperature and speed control in the process of the present invention.

图1为本发明的工艺过程温度、转速控制示意图。

[n0026]

Figure 2 shows the XRD patterns of calcium-doped barium titanate powder synthesized in Example 1, Comparative Example 1, and Comparative Example 2 of the present invention (where R1, R2, and R3 correspond to Example 1, Comparative Example 1, and Comparative Example 2, respectively, and the right side is a magnified view of the 45° peak).

图2为为本发明实施例1、对比例1、对比例2合成的钙掺杂钛酸钡粉体的XRD图谱(其中R1、R2、R3分别对应实施例1、对比例1、对比例2，右侧为45°峰放大图)。

[n0027]

Figure 3 shows an SEM image of the calcium-doped barium titanate powder synthesized in Example 1 of the present invention, as well as the particle size distribution and average particle size statistically analyzed from the SEM image.

图3为本发明实施例1合成的钙掺杂钛酸钡粉体的SEM照片以及根据SEM照片统计的粒径分布及平均粒径。

[n0028]

Figure 4 shows an SEM image of the calcium-doped barium titanate powder synthesized in Comparative Example 1 of this invention, as well as the particle size distribution and average particle size statistically analyzed from the SEM image.

图4为本发明对比例1合成的钙掺杂钛酸钡粉体的SEM照片以及根据SEM照片统计的粒径分布及平均粒径。

[n0029]

Figure 5 shows the SEM images of the calcium-doped barium titanate powder synthesized in Comparative Example 2 of this invention, as well as the particle size distribution and average particle size statistically analyzed from the SEM images.

图5为本发明对比例2合成钙掺杂钛酸钡粉体的SEM照片以及根据SEM照片统计的粒径分布及平均粒径。

[0034]

Detailed Implementation

具体实施方式

[n0030]

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。

[n0031]

In the following embodiments, the characteristics of the calcium-doped barium titanate powder were characterized using the following detection techniques or methods:

下述实施例中，利用以下检测技术或手段对产物钙掺杂的钛酸钡粉体的特性进行表征：

[n0032]

(1) X-ray diffraction patterns were collected in the range of 10-80° using a Rigaku SmartLab X-ray diffractometer manufactured by Rigaku Corporation with a step size of 0.02° and an integration time of 2s. The lattice constant ratio (c/a) of the calcium-doped barium titanate product was calculated by Rietveld method using FullProf Suite software for structural refinement.

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(1)利用日本理学株式会社生产的日本理学SmartLab型号的X射线衍射仪以步长0.02°、积分时间为2s的参数在10-80°范围内采集X射线衍射图谱，通过FullProf Suite软件采用Rietveld法进行结构精修计算产物钙掺杂的钛酸钡的晶格常数比(c/a)。

[n0033]

(2) Topographic images were taken using a SEM 450 field emission scanning electron microscope manufactured by FEI Corporation of the United States.

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(2)使用美国FEI公司生产的SEM 450型号场发射扫描电镜拍摄形貌照片。

[n0034]

(3) Using Nanomeasure 1.12 software, sample and measure the particles in the electron microscope images, count 100 to 150 particles, and make a particle size distribution map.

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(3)使用Nanomeasure 1.12软件，对电镜照片中的颗粒进行取样测量，统计100～150个颗粒，作出粒径分布图。

[n0035]

In the examples or comparative examples below, the raw materials used, calcium carbonate with a particle size of about 1 μm, barium carbonate with a particle size of about 750 nm, and titanium dioxide with a particle size of about 100 nm.

在下述实施例或对比例中，所使用的原料碳酸钙的粒度约为1μm，碳酸钡的粒度约为750nm，二氧化钛的粒度约为100nm。

In order to ensure that the raw material powder is mixed evenly and in full contact, the raw material powder is mixed evenly by ball milling. The ball milling media used is zirconium oxide. In other embodiments, roller milling, grinding, sand milling and other methods can also

be used to mix the raw material powder evenly, all of which are included within the protection scope of this invention.

为了使原料粉体能够混合均匀，充分接触，原料粉体通过球磨的方式均匀混合，所使用的球磨介质为氧化锆，在其它实施例中也可以用过辊磨、研磨、砂磨等方式使原料粉体混合均匀，均包括在本发明的保护范围内。

[n0036]

Example 1

实施例1

[n0037]

a.

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a.

With the rotary kiln cavity placed horizontally and connected to the atmosphere, barium carbonate, titanium dioxide, and calcium carbonate (molar ratio of TiO24:BaCO25:CaCO26 = 1: 0.9:0.1) were ball-milled at 480 rpm for 24 hours using zirconium oxide media (mass ratio of

material:zirconium balls:water = 1:2:1). 15g of the uniformly mixed raw material powder was weighed and pushed into the middle of the laboratory rotary kiln cavity using a shovel.

在回转炉管腔水平放置且与大气接通的情况下，将碳酸钡、二氧化钛、碳酸钙(摩尔比为TiO₂:BaCO₃:CaCO₃＝1:0.9:0.1)使用氧化锆介质在480转下球磨24h(质量比，物料：锆球：水＝1:2:1)，将混合均匀的原料粉体称取15g，用铲子推入实验室用回转炉管腔中部；

[n0038]

b.

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b.

The heating rate of the laboratory rotary furnace is set to 10°C/min, from the initial temperature to 1000°C. After holding at 1000°C for 2 hours, the temperature is reduced to the initial temperature at a rate of 10°C/min and then stopped. The rotation speed of the furnace cavity is set to 4 revolutions/minute.

设置实验室用回转炉的升温速率为10°C/min，从初始温度升至1000°C，设定在1000°C保温时间2h后，以10°C/min速率，降温到初始温度停止；设置炉腔旋转速度为4转/分钟；

[n0039]

d.

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d.

Start the program;

启动程序；

[n0040]

e.

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e.

After the furnace temperature reaches 1000°C and has been held for 1 hour, the rotation speed of the rotary kiln is set to 10 revolutions per minute.

待炉腔温度升至1000°C并且已保温1h后，设置回转炉的炉腔旋转速度为10转/分钟。

[n0041]

After the experiment, the product powder was collected using a receiving shovel, and the sample code was recorded as R1.

实验完成后用接料铲收集产物粉体，样品代号记为R1。

[n0042]

The rotary kiln speed control unit used in this embodiment and the following comparative examples does not include programming function. Therefore, parameters such as heating temperature, heating rate, holding time and initial speed can be set once before the rotary kiln is started. Step e, i.e., the setting of the second speed segment, needs to be manually adjusted midway.

本实施例以及下述对比例中所使用的回转炉转速控制单元不包含编程功能，因此加热温度、升温速率、保温时长以及初始转速等参数可在回转炉运转前一次设定完毕，步骤e即第二段转速的设定需要中途手动调整。

When implementing this invention using other rotary kilns, such as those with programmable speed control units, all parameters can be set during the initial setup process.

在使用其它诸如转速控制单元可供编程的回转炉实施本发明时，可在初始设置过程中将一应参数设置完毕。

[n0043]

Comparative Example 1

对比例1

[n0044]

a.

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a.

Barium carbonate, titanium dioxide, and calcium carbonate (molar ratio of TiO27:BaCO28: CaCO29 = 1:0.9:0.1) were ball-milled at 480 rpm for 24 hours using zirconium oxide media (mass ratio of material:zirconium balls:water = 1:2:1). 15g of the resulting powder was weighed and pushed into the middle of the chamber of a laboratory rotary kiln using a shovel.

将碳酸钡与二氧化钛、碳酸钙(摩尔比为TiO₂:BaCO₃:CaCO₃=1:0.9:0.1)使用氧化锆介质在480转下球磨24h(质量比，物料：锆球：水＝1:2:1)混合均匀的原料粉体称取15g，用铲子推入实验室用回转炉管腔中部；

[n0045]

b.

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b.

The heating rate of the laboratory rotary furnace is set to 10°C/min, from the initial temperature to 1000°C. After holding at 1000°C for 2 hours, the temperature is reduced to the initial temperature at a rate of 10°C/min and then stopped. The rotation speed of the furnace cavity is set to 4 revolutions/minute.

设置实验室用回转炉的升温速率为10°C/min，从初始温度升至1000°C，设定在1000°C保温时间2h后，以10°C/min速率，降温到初始温度停止；设置炉腔旋转速度为4转/分钟；

[n0046]

c.

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c.

Start the program.

启动程序。

[n0047]

After the experiment, the product powder was collected using a receiving shovel, and the sample code was recorded as R2.

实验完成后用接料铲收集产物粉体，样品代号记为R2。

[n0048]

Comparative Example 2

对比例2

[n0049]

a.

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a.

Barium carbonate, titanium dioxide, and calcium carbonate (molar ratio of TiO30:BaCO31: CaCO32 = 1:0.9:0.1) were ball-milled at 480 rpm for 24 hours using zirconium oxide media (mass ratio of material:zirconium balls:water = 1:2:1). 15g of the resulting powder was weighed and placed in a crucible, then pushed into the middle of the chamber of a laboratory muffle furnace using a shovel.

将碳酸钡与二氧化钛、碳酸钙(摩尔比为TiO₂:BaCO₃:CaCO₃=1:0.9:0.1)使用氧化锆介质在480转下球磨24h(质量比，物料：锆球：水＝1:2:1)混合均匀的原料粉体称取15g盛放在坩埚中，用铲子推入实验室用马弗炉腔室中部；

[n0050]

b.

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b.

The heating rate of the laboratory muffle furnace was set to 10°C/min. The temperature was raised from the initial temperature to 1000°C and held for 2 hours. After the holding period, the temperature was lowered from 1000°C to the initial temperature at a rate of 10°C/min, and then the program was terminated.

设置实验室用马弗炉的升温速率为10°C/min，从初始温度升至1000°C保温2h，保温结束后以10°C/min从1000°C降温到初始温度后终止程序；

[n0051]

c.

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c.

Start the program;

启动程序；

[n0052]

After the experiment, the product powder was collected using a receiving shovel, and the sample code was recorded as R3.

实验完成后用接料铲收集产物粉体，样品代号记为R3。

[n0053]

Results Explanation

结果说明

[n0054]

As shown in Figures 3-5 and Table 1, the average particle size of sample R1 (with a rotation speed of 4 rpm followed by 10 rpm in Example 1) is compared with that of sample R2 (with a constant rotation speed of 4 rpm in Comparative Example 1). The average particle size of R1 (1.32 μm) is smaller than that of R2 (1.34 μm). At the same time, the tetragonality (i.e., c/a value) of R1 is 1.0101 and that of R2 is 1.00993. R1 is superior to R2 in all aspects, indicating that the low-high two-stage rotation speed method is better than the constant rotation speed process.

如图3-5以及表1所示，实施例1转速为先4rpm后10rpm的样品R1平均粒径与对比例1转速恒为4rpm的样品R2对比，R1的平均颗粒尺寸1.32μm小于R2的平均颗粒尺寸1.34μm，同时四方性(即c/a值)R1为1.0101，R2为1.00993，R1全面优于R2，说明低-高两段转速的方法优于恒定转速的工艺。

[n0055]

Compared with the sample R3 calcined in a muffle furnace in Comparative Example 2, the sample R1 with a rotation speed of 4 rpm followed by 10 rpm in Example 1 shows, from the

scanning electron microscope images, that the powder particles of R3 are severely agglomerated, the grain boundaries are in close contact, there are signs of sintering, and huge hexagonal particles have appeared.

实施例1转速为先4rpm后10rpm的样品R1与对比例2马弗炉中煅烧的样品R3相比，从扫描电镜的照片中可以看到，R3的粉体颗粒团聚十分严重，晶界紧密接触，已经有烧结迹象，出现了六边形的巨大的颗粒。

Although R1 has slightly larger particle size, it is more tetragonal and shows no signs of sintering, exhibiting better dispersibility.

R1虽然颗粒尺寸稍大一些，但四方性更高，而且无烧结迹象，分散性较好。

[n0056]

Table 1 summarizes the lattice parameters and average particle size of R1 (Example 1), R2 (Comparative Example 1), and R3 (Comparative Example 2).

表1R1(实施例1)、R2(对比例1)、R3(对比例2)的晶格参数和平均粒径汇总。

[n0058]

In summary, the method provided by this invention successfully prepared calcium-doped barium titanate powder with high tetragonality, uniform particle size, and good dispersibility, providing new technical support for the preparation of calcium-doped barium titanate powder.

综上所述本发明提供的方法成功制备了高四方性、粒度均匀、分散性好的钙掺杂钛酸钡粉体，为制备钙掺杂钛酸钡粉体提供了一种新的技术支持。

[n0059]

The above description is merely a preferred embodiment of the present invention and does not limit the patent scope of the present invention. Any equivalent transformations made based on the content of the present invention's specification and drawings, or direct or indirect applications in other related technical fields, are similarly included within the patent protection scope of the present invention.

以上所述仅为本发明的优选实施例，并非因此限制本发明的专利范围，凡是利用本发明说明书及附图内容所作的等效变换，或直接或间接运用在其他相关的技术领域，均同理包括在本发明的专利保护范围内。