Notice

DESCRIPTION CN115959703A

Calcium-doped barium titanate powder, preparation method and uses

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钙掺杂钛酸钡粉体、制备方法及其用途

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of dielectric ceramic powder preparation technology, specifically to calcium-doped barium titanate powder, its preparation method, and its applications.

本发明涉及电介质陶瓷粉体制备技术领域，具体涉及钙掺杂钛酸钡粉体、制备方法及其用途。

[0003]

Background Technology

背景技术

[n0002]

Multilayer ceramic capacitors (MLCCs) are among the most widely used and most important electronic components in electronic devices, often referred to as the "rice of industry." They possess high capacitance, high reliability, and excellent high-frequency characteristics. To meet the development requirements of high capacitance, high temperature, high voltage, high frequency, high reliability, and miniaturization of multilayer ceramic capacitors in the 5G era, developing high-performance dielectric ceramic powders suitable for industrial production and application has become an urgent task.

多层陶瓷电容器(MLCC)是电子设备中使用最多也是最重要的电子元器件之一，被称为“产业之米”，其具有高电容、高可靠性和出色的高频特性，为了满足5G时代多层陶瓷电容器的高容、高温、高压、高频、高可靠性及小型化“五高一小”的发展需求，开发适合工业化生产及应用的高性能电介质陶瓷粉体成为当务之急。

MLCCs are multilayer chip capacitors composed of ceramic dielectric and metal internal electrodes stacked together and encapsulated with end electrodes. By selecting dielectric materials with higher dielectric constants, smaller ceramic dielectric powder particles, and increasing the number of dielectric layers, the performance requirements of rapidly developing electronic devices can be met.

MLCC是由陶瓷介质和金属内电极叠成，端电极封装组成的片式多层电容器，通过选择具有更高介电常数、陶瓷介质填充粉体更小的介电材料以及增加介电层的数量，可以满足快速发展的电子设备的性能需求。

Therefore, the synthesis of ceramic powders for dielectric layers and internal metal electrodes is crucial.

因此，用于介电层和金属内部电极的陶瓷粉体的合成至关重要。

[n0003]

In MLCCs, the commonly used dielectric ceramic filler powder is BaTiO2-based material.

在MLCC中，常用的电介质陶瓷填充粉体是BaTiO₃基材料。

The dielectric constant of high-dielectric materials is related to their microstructure, i.e., tetragonality. Unmodified BaTiO2 ceramic powder exhibits limited tetragonality and a narrower operational temperature range for MLCCs. To adapt to the rapid development of the electronics industry, it is necessary to develop dielectric materials with better performance. Improving the preparation process and doping barium titanate-based materials to enhance their performance are two of the most common methods. Ca-doped BaTiO3-based materials (Ba4Ca5TiO6, BCT) are considered the most important candidate materials for lead-free optoelectronic modulators and memory devices. Furthermore, BCT materials possess a more stable tetragonal ferroelectric phase, exhibiting better temperature-capacitance characteristics and a higher dielectric constant, which can broaden the operational temperature range of barium titanate for MLCCs.

高介电材料的介电常数与材料的微观结构即四方性有关，其中BaTiO₃陶瓷粉体在未经改性时，四方性以及MLCC的温度范围的可操作区间较小，为了适应电子产业的快速发展，需要开发性能更好的介电材料，其中改进制备工艺和对钛酸钡基进行掺杂改性以改善钛酸钡基材料的性能是两种最常用的方法，其中，Ca掺杂的BaTiO₃基(Ba_{1-X}Ca_xTiO₃，BCT)被认为是无铅光电调制器和存储器件的最重要的候选材料，且BCT材料具有更稳定的四方铁电相，具有更好的容温特性和更高的介电常数，可拓宽钛酸钡用于MLCC的温度可操作区间。

[0006]

Summary of the Invention

发明内容

[n0004]

To address the aforementioned technical problems, this invention provides a calcium-doped barium titanate powder, its preparation method, and its applications. By improving the preparation process of barium titanate powder and doping it with Ca, the resulting barium titanate-based powder exhibits excellent tetragonality and can be applied to the dielectric layer of multilayer ceramic capacitors.

针对上述技术问题，本发明提供一种钙掺杂钛酸钡粉体、制备方法及其用途，通过改进钛酸钡粉体的制备工艺，在钛酸钡粉体中掺杂Ca元素，得到的钛酸钡基粉体具有良好的四方性，可应用于多层陶瓷电容器的电介质层。

[n0005]

To achieve the above objectives, the present invention is implemented through the following technical solution:

为了实现上述目的，本发明通过以下技术方案实现：

[n0006]

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：

[n0007]

Step (1), prepare powder I by atmospheric pressure hydrothermal method: add the first Ba source to water, stir to dissolve, then add an aqueous dispersion containing Ti source, stir and react at a certain temperature, and then dry to obtain powder I;

步骤(1)，常压水热法制备粉体I：将第一Ba源加入水中，搅拌溶解，再加入含有Ti源的水分散液，在一定温度下搅拌反应后干燥得到粉体I；

[n0008]

Step (2), solid-state method to prepare calcium-doped barium titanate powder: After adding the second Ba source and Ca source to powder I, mix and ball mill, dry and sieve, grind, and finally calcine to obtain calcium-doped barium titanate powder;

步骤(2)，固相法制备钙掺杂钛酸钡粉体：将粉体I中加入第二Ba源和Ca源后混合球磨，干燥过筛后研磨，最后进行煅烧得到钙掺杂钛酸钡粉体；

[n0009]

In step (1), the molar ratio of Ba contained in the first Ba source to that in the second Ba source is 0.05 to 0.5, and the molar ratio of the total Ba contained in the first Ba source and the second Ba source to that contained in the Ti source is 0.99 to 1.01. In step (2), the molar ratio of Ca contained in the Ca source to that in the first Ba source and the second Ba source is 0.01 to 0.5.

步骤(1)中，第一Ba源与第二Ba源含有的Ba的摩尔比为0.05～0.5，第一Ba源与第二Ba源含有的总Ba与Ti源中含有的Ti的摩尔比为：0.99-1.01，步骤(2)中，Ca源含有的Ca与第一Ba源和第二Ba源含有的总Ba的摩尔比为0.01～0.5。

[n0010]

In some specific implementations, in step (1), the molar ratio of Ba contained in the first Ba source and the second Ba source is 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 or any value between them.

在某些具体的实施方式中，步骤(1)中，第一Ba源与第二Ba源含有的Ba的摩尔比为0.05、0.1、0.15、0.2、0.25、0.3、0.35、0.4、0.45、0.5或它们之间的任意数值。

[n0011]

In some specific implementations, in step (1), the molar ratio of the total Ba contained in the first Ba source and the second Ba source to the Ti contained in the Ti source is 0.99, 1.00, 1.01 or any value between them.

在某些具体的实施方式中，步骤(1)中，第一Ba源与第二Ba源含有的总Ba与Ti源中含有的Ti的摩尔比为0.99、1.00、1.01或它们之间的任意值。

[n0012]

In some specific embodiments, in step (2), the molar ratio of Ca contained in the Ca source to the total Ba contained in the first Ba source and the second Ba source is 0.01, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 or any value between them.

在某些具体的实施方式中，步骤(2)中，Ca源含有的Ca与第一Ba源和第二Ba源含有的总Ba的摩尔比为0.01、0.1、0.15、0.2、0.25、0.3、0.35、0.4、0.45、0.5或它们之间的任意数值。

[n0013]

Furthermore, in step (1), the first Ba source is a water-soluble Ba source, and the Ti source is TiO₂ with anatase phase; the stirring reaction environment is alkaline with pH>10.

进一步地，步骤(1)中，第一Ba源为水溶性Ba源，Ti源为具有锐钛矿相的TiO₂；搅拌反应环境为碱性，PH>10。

[n0014]

In some specific embodiments, the first Ba source is barium hydroxide, barium nitrate, barium chloride, or any other water-soluble Ba source, which can be used alone or in any combination.

在某些具体的实施方式中，第一Ba源为氢氧化钡、硝酸钡、氯化钡或其它任意水溶性Ba源，可以单独使用也可以任意混合使用。

[n0015]

Furthermore, in step (2), the second Ba source is BaCO₃, and the Ca source is CaCO₃.

进一步地，步骤(2)中，第二Ba源为BaCO₃，Ca源为CaCO₃。

[n0016]

Furthermore, in step (1), after adding the aqueous dispersion containing Ti source, the stirring reaction temperature is 80°C-120°C, and the stirring reaction time is 30min-12h.

进一步地，步骤(1)中，加入含有Ti源的水分散液后搅拌反应温度为80°C-120°C，搅拌反应时间为30min-12h。

[n0017]

In some specific embodiments, in step (1), after adding the aqueous dispersion containing the Ti source, the stirring reaction temperature is 80°C, 90°C, 100°C, 110°C, 120°C or any temperature between them.

在某些具体的实施方式中，步骤(1)中，加入含有Ti源的水分散液后搅拌反应温度为80°C、90°C、100°C、110°C、120°C或它们之间的任意温度。

[n0018]

In some specific embodiments, in step (1), the stirring reaction time is 30 min, 1 h, 3 h, 5 h, 7 h, 10 h, 12 h or any reaction time between them.

在某些具体的实施方式中，步骤(1)中，搅拌反应时间为30min、1h、3h、5h、7h、10h、12h或它们之间的任意反应时间。

[n0019]

Furthermore, in step (2), the calcination temperature is 300°C-1300°C, the calcination time is 30min-4h, and the heating rate is 2～15°C/min.

进一步地，步骤(2)中，煅烧温度为300℃-1300℃，煅烧时间为30min-4h，升温速率是2～15℃/min。

[n0020]

In some specific embodiments, in step (2), the calcination temperature is 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C, 1200°C, 1300°C or any temperature between them.

在某些具体的实施方式中，步骤(2)中，煅烧温度为300℃、400℃、500℃、600℃、700℃、800℃、900℃、1000℃、1100℃、1200℃、1300℃或它们之间的任意温度。

[n0021]

In some specific embodiments, in step (2), the calcination time is 30 min, 1 h, 2 h, 3 h, 4 h or any reaction time in between.

在某些具体的实施方式中，步骤(2)中，煅烧时间为30min、1h、2h、3h、4h或它们之间的任意反应时间。

[n0022]

In some specific embodiments, in step (2), the heating rate is 2°C/min, 3°C/min, 4°C/min, 5°C/min, 7°C/min, 10°C/min, 12°C/min, 15°C/min or any heating rate between them.

在某些具体的实施方式中，步骤(2)中，升温速率为2℃/min、3℃/min、4℃/min、5℃/min、7℃/min、10℃/min、12℃/min、15℃/min或它们之间的任意升温速率。

[n0023]

Furthermore, in step (2), the ball milling media are zirconium beads and deionized water, and the ball milling time is 24 hours. In the technical solution of the present invention, the ball milling operation makes the hydrothermal product of step (1) mixed evenly with the second Ba source and Ca source.

进一步地，步骤(2)中，球磨介质为锆珠和去离子水，球磨时间为24h，本发明的技术方案中，球磨操作使得步骤(1)的水热产物与第二Ba源和Ca源混合均匀。

[n0024]

Furthermore, in step (2), the sieving operation is performed using a 200-mesh sieve.

进一步地，步骤(2)中，过筛操作使用200目筛进行。

[n0025]

The second aspect of the present invention provides calcium-doped barium titanate powder obtained by the above preparation method.

本发明第二方面提供上述制备方法获取的钙掺杂钛酸钡粉体。

In the technical solution of the present invention, the calcium-doped barium titanate powder obtained by the above preparation method has Ca element in the Ca source that can partially replace the A site of the barium titanate group.

本发明的技术方案中，经过上述制备方法得到的钙掺杂钛酸钡粉体，Ca源中的Ca元素能够部分取代钛酸钡基的A位。

[n0026]

Furthermore, the chemical structural formula of the calcium-doped barium titanate powder is Ba_xCa_{1-x}TiO₃, where x is 0.8 to 0.9, and its tetragonality c/a = 1.009-1.011.

进一步地，所述钙掺杂钛酸钡粉体的化学结构式为Ba_xCa_{1-x}TiO₃，其中x为0.8～0.9，其四方性c/a＝1.009-1.011。

[n0027]

In some specific embodiments, the x in the chemical structural formula Ba_xCa_{1-x}TiO₃ of the calcium-doped barium titanate powder is 0.8, 0.81, 0.9 or any value between them, and its tetragonality c/a is 1.009, 1.010, 1.011 or any value between them.

在某些具体的实施方式中，所述钙掺杂钛酸钡粉体的化学结构式Ba_xCa_{1-x}TiO₃中的x为0.8、0.81、0.9或它们之间的任意值，其四方性c/a为1.009、1.010、1.011或它们之间的任意值。

[n0028]

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, the use of barium titanate powder in the preparation of electronic components, wherein the electronic components are 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，钛酸钡粉体用于制备电子元器件的用途，所述电子元器件为多层陶瓷电容器。

[n0029]

The above technical solution has the following advantages or beneficial effects:

上述技术方案具有如下优点或者有益效果：

[n0030]

This invention employs a atmospheric pressure hydrothermal assisted solid-state synthesis method. First, at atmospheric pressure and low hydrothermal temperature, a soluble Ba source and a Ti source seeded with TiO₂ are dispersed in an aqueous solution and stirred for reaction. Then, a second Ba source and a Ca source are mixed with the above hydrothermal product using a solid-state synthesis method, ball-milled, dried, and calcined to obtain highly tetragonal calcium-doped barium titanate powder. This invention improves the tetragonality and dielectric constant of barium titanate powder by Ca doping the barium titanate material and adjusting the reaction temperature and raw material ratio, allowing Ca to partially replace the A-site of the barium titanate group. Furthermore, by adjusting the raw material ratio, a suitable final stoichiometric product can be obtained, and the particle properties of the product can be controlled by changing the process.

本发明采用常压水热辅助固相合成的制备方法，首先在常压低水热温度下，使用可溶性的Ba源和以TiO₂为种子的Ti源分散在水溶液中，搅拌反应；然后用固相合成法将第二Ba源，Ca源与上述水热产物混合球磨，干燥煅烧即可得到高四方性的钙掺杂钛酸钡粉体，本发明通过对钛酸钡材

料进行Ca掺杂，通过调整反应温度和原料配比，使得Ca元素部分取代钛酸钡基的A位，提高了钛酸钡粉体的四方性和介电常数，且通过调整原料配比，得到合适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等优点。

The present invention features a simple process, readily available raw materials, and high product stability, providing new technical support for the preparation of ceramic powders in high-capacitance multilayer ceramic capacitors.

本发明工艺简单，原料易得，产品稳定性高，为制备高电容的多层陶瓷电容器中的陶瓷粉体提供了一种新的技术支持。

[0034]

Attached Figure Description

附图说明

[n0031]

Figure 1 is an XRD pattern of the calcium-doped barium titanate powder synthesized in Example 1 of the present invention;

图1是本发明实施例1合成的钙掺杂钛酸钡粉体的XRD图；

[n0032]

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

图2是本发明实施例1合成的钙掺杂钛酸钡粉体的SEM图；

[n0033]

Figure 3 is the XRD pattern of the calcium-doped barium titanate powder synthesized in Example 2 of the present invention;

图3是本发明实施例2合成的钙掺杂钛酸钡粉体的XRD图；

[n0034]

Figure 4 is a SEM image of the calcium-doped barium titanate powder synthesized in Example 2 of the present invention.

图4是本发明实施例2合成的钙掺杂钛酸钡粉体的SEM图。

[0039]

Detailed Implementation

具体实施方式

[n0035]

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。

[n0036]

The technical solution of this invention is to design a method for preparing calcium-doped barium titanate powder. This method is mainly based on solid-state method and supplemented by atmospheric pressure hydrothermal method. Doping barium titanate powder with Ca element can greatly improve the dielectric constant of barium titanate-based materials.

本发明的技术方案在于设计一种钙掺杂钛酸钡粉体的制备方法，该方法以固相法为主，常压水热法为辅，对钛酸钡粉体掺杂Ca元素，可大大提高钛酸钡基材料的介电常数。

[n0037]

In the following embodiments:

下述实施例中：

[n0038]

(1) The selected raw materials are Ba(OH)NER17・8HNER18O, anatase TiONER19, BaCONER20 and CaCONER21;

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(1)所选原料为Ba(OH)₂・8H₂O，锐钛矿相TiO₂，BaCO₃和CaCO₃；

[n0039]

(2) Control the addition ratio of raw materials Ba(OH)2・8H2O and BaCO24, and change the addition ratio of CaCO25.

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(2)控制原料Ba(OH)₂・8H₂O和BaCO₃的加入比例，改变CaCO₃的加入比例；

[n0040]

(3) In the atmospheric pressure hydrothermal method, Ba(OH)₂・8H₂O is first dissolved in water, heated and stirred, and then TiO₂ of the anatase phase is added. Water is then added to the dispersion, the heating temperature is set, and the reaction is stirred continuously for several hours. The pH of the stirring reaction is >10.

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(3)在常压水热法中，先将Ba(OH)₂・8H₂O溶于水中，加热搅拌后，再加入锐钛矿相的TiO₂，继续加水于分散液中，设置加热温度，持续搅拌反应数小时，搅拌反应的pH＞10；

[n0041]

(4) When the hydrothermal reaction at normal pressure is over, transfer the hydrothermal product to a ball mill jar, dry it, and add a certain proportion of BaCO₃ and CaCO₃. Use deionized water and zirconium beads as the ball milling medium to carry out solid-phase synthesis and mix and ball mill for several hours.

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(4)待常压水热反应结束时，将水热产物转移至球磨罐中，干燥后加入一定比例的BaCO₃，CaCO₃，以去离子水和锆珠为球磨介质，进行固相合成，混合球磨数小时；

[n0042]

(5) After ball milling, the product is dried, sieved and ground, and an appropriate amount of powder is calcined.

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(5)球磨结束后，对产物干燥后过筛并研磨处理，取适量粉体煅烧。

[n0043]

Example 1:

实施例1：

[n0044]

In this embodiment, the molar ratio of Ba/Ca in the total Ba source and Ca source during the entire reaction process is 0.9/0.1, the molar ratio of Ba(OH)31・8H32O to BaCO33 is 0.25/0.75, the molar ratio of Ba/Ti in the entire reaction is 1, and the materials are prepared according to the molar ratio of Ba(OH)34・8H35O:BaCO36:CaCO37 = 0.225:0.675:0.1, and the obtained barium titanate powder is Ba38Ca39TiO40.

本实施例中，整个反应过程中的总Ba源与Ca源中的Ba/Ca的摩尔比为0.9/0.1，Ba(OH)₂・8H₂O与BaCO₃的摩尔比为0.25/0.75，整个反应中的Ba/Ti的摩尔比为1，按照Ba(OH)₂・8H₂O：BaCO₃：CaCO₃＝0.225：0.675：0.1的摩尔比例进行配料，获得的钛酸钡粉体为Ba_{0.9}Ca_{0.1}TiO₃。

First, weigh 7.2427 g of Ba(OH)O into a three-necked flask, add 25 ml of water, and stir continuously for 30 min. Then, weigh 0.1 mol of 8.003 g of TiO and 15 ml of water into the aqueous dispersion of Ba. Set the heating temperature to 100°C and perform a hydrothermal reaction at atmospheric pressure for 6 h. After the hydrothermal reaction is completed, transfer the hydrothermal product to a ball mill jar for drying, and weigh out the product according to the specified proportion. BaCO₃ and CaCO₃ were mixed in a ball mill jar, with zirconium beads and deionized water as the milling media. The hydrothermal product was then mixed with BaCO₃ and CaCO₃ and ball-milled for 24 hours. After ball milling, the mixture was dried, ground, and passed through a 200-mesh sieve. Approximately 1 g of the powder was placed in a muffle furnace and calcined at 950°C-1100°C with a heating rate of 5°C/min and a holding time of 2 hours.

先称取7.2427g的Ba(OH)₂・8H₂O于三口烧瓶中，加入25ml的水，持续搅拌30min后，按比例称取0.1mol的8.003g的TiO₂和15ml的水于Ba的水分散液中，设置加热温度为100°C，常压水热反应6h；水热反应结束后，将水热产物转移至球磨罐中干燥，称取按照比例配比的BaCO₃和CaCO₃于球磨罐中，球磨介质为锆珠和去离子水，将所述的水热产物与BaCO₃和CaCO₃混合球磨24h；待球磨结束后，对混合进行干燥后，研磨并过200目筛，取约1g的粉体置于马弗炉中在950°C-1100°C煅烧，升温速率为5°C/min，保温时间是2h。

Figure 1 is the XRD pattern of Ba_{0.9}Ca_{0.1}TiO₃ powder prepared by calcining the calcium-doped barium titanate powder synthesized in this embodiment at 950°C, 1000°C, and 1100°C for 2h. Figure 2 is the SEM image of Ba<sub>0.9<

/sub>Ca_{0.1}TiO₃ powder prepared by calcining the calcium-doped barium titanate powder synthesized in this embodiment at 1000°C and 1100°C for 2h.

图1是本实施例合成的钙掺杂钛酸钡粉体在950°C、1000°C、1100°C煅烧2h后制备的Ba_{0.9}Ca_{0.1}TiO₃粉体的XRD图，图2是本实施例合成的钙掺杂钛酸钡粉体在1000°C和1100°C煅烧2h后制备的Ba_{0.9}Ca_{0.1}TiO₃粉体的SEM图。

[n0045]

Example 2:

实施例2：

[n0046]

In this embodiment, the molar ratio of Ba/Ca in the Ba source and Ca source during the entire reaction process is 0.8/0.2, the molar ratio of Ba(OH)・8HO to BaCO ...

本实施例中，整个反应过程中的Ba源与Ca源中的Ba/Ca的摩尔比为0.8/0.2，Ba(OH)₂・8H₂O与BaCO₃的摩尔比为0.25/0.75，整个反应中的Ba/Ti的摩

尔比为1，按照Ba(OH)₂・8H₂O：BaCO₃：CaCO₃＝0.2：0.6：0.2的摩尔比例进行配料，制备的钙掺杂钛酸钡粉体为Ba_{0.8}Ca_{0.2}TiO₃。

First, weigh 6.4381 g of Ba(OH)・NER64・8HO into a three-necked flask, add 25 ml of water, and stir continuously for 30 min. Then, weigh 8.003 g of TiO・NER66 and 15 ml of water into the aqueous dispersion of Ba. Set the heating temperature to 100°C and perform a hydrothermal reaction at atmospheric pressure for 6 h. After the hydrothermal reaction is completed, transfer the hydrothermal product to a ball mill jar for drying, and weigh out the product according to the specified proportions. BaCO₃ and CaCO₃ were placed in a ball mill jar, with zirconium beads and deionized water as the milling media. The hydrothermal product was mixed with BaCO₃ and CaCO₃ and ball-milled for 24 hours. After ball milling, the mixture was dried, ground, and passed through a 200-mesh sieve. Approximately 1g of powder was placed in a muffle furnace and calcined at 950°C-1100°C with a heating rate of 5°C/min and a holding time of 2 hours.

先称取6.4381g的Ba(OH)₂・8H₂O于三口烧瓶中，加入25ml的水，持续搅拌30min后，再按比例称取8.003g的TiO₂和15ml的水于Ba的水分散液中，设置加热温度为100°C，常压水热反应6h；水热反应结束后，将水热产物转移至球磨罐中干燥，称取按照比例配比的BaCO₃和CaCO₃于球磨罐中，球磨介质为锆珠和去离子水，将所述的水热产物与BaCO₃和CaCO₃混合球磨24h；待球磨结束后，对混合

物进行干燥后，研磨并过200目筛，取约1g粉体置于马弗炉中在950°C-1100°C煅烧，升温速率为5°C/min，保温时间是2h。

Figure 3 is the XRD pattern of Ba_{0.8}Ca_{0.2}TiO₃ powder prepared by calcining the powder at 950°C, 1000°C, and 1100°C for 2h in this embodiment. Figure 4 is the SEM pattern of Ba_{0.8}Ca_{0.2}TiO₃ powder prepared by calcining the powder at 1000°C and 1100°C for 2h in this embodiment.

图3是本实施例的粉体在950°C、1000°C、1100°C煅烧2h后制备的Ba_{0.8}Ca_{0.2}TiO₃粉体的XRD图，图4是本实施例的粉体在1000°C和1100°C煅烧2h后制备的Ba_{0.8}Ca_{0.2}TiO₃粉体的SEM图。

[n0047]

Comparative example:

对比例：

[n0048]

In this comparative example, the molar ratio of Ba/Ca in the Ba source and Ca source throughout the reaction process is 1, the molar ratio of Ba(OH)・8HO to BaCO is 0.25/0.75, the molar ratio of Ba/Ti throughout the reaction is 1, and the materials are prepared according to the molar ratio of Ba(OH)・8HO:BaCO:CaCO = 0.25:0.75:0, resulting in barium titanate powder of type BaTiO.

本对比例中，整个反应过程中的Ba源与Ca源中的Ba/Ca的摩尔比为1，Ba(OH)₂・8H₂O与BaCO₃的摩尔比为0.25/0.75，整个反应中的的Ba/Ti的摩尔比为1，按照Ba(OH)₂・8H₂O：BaCO₃：CaCO₃＝0.25：0.75：0的摩尔比例进行配料，制备的钛酸钡粉体为BaTiO₃。

First, weigh 8.0474 g of Ba(OH)NER85・8HNER86O into a three-necked flask, add 25 ml of water, and stir continuously for 30 min. Then, weigh a certain mass of TiONER87 and 15 ml of water into the aqueous dispersion of Ba. Set the heating temperature to 100°C and perform a hydrothermal reaction at atmospheric pressure for 6 h. After the hydrothermal reaction is completed, transfer the hydrothermal product to a ball mill jar for drying. Weigh BaCONER88 according to the specified ratio into the ball mill jar. The ball milling media are zirconium beads and deionized water. Mix the hydrothermal product with BaCONER89 and ball mill for 24 h. After ball milling, dry the mixture, grind it, and pass it through a 200-mesh sieve. Take about 1 g of the powder and place it in a muffle furnace for calcination at 950°C, 1000°C, and 1050°C, with a heating rate of 5°C/min and a holding time of 2 h.

先称取8.0474g的Ba(OH)₂・8H₂O于三口烧瓶中，加入25ml的水，持续搅拌30min后，按比例称取一定质量的TiO₂和15ml的水于Ba的水分散液中，设置加热温度为100℃，常压水热反应6h；水热反应结束后，将水热产物转移至球磨罐中干燥，称取按照比例配比的BaCO₃于球磨罐中，球磨介质为锆珠和去离子水，将所述的水热产物与BaCO₃混合球磨24h；待球磨结束后，对混合进行干燥后，研磨并过200目筛，取约1g的粉体置于马弗炉中在950℃、1000℃、1050℃煅烧，升温速率为5℃/min，保温时间是2h。

Table 1.

表1.

These are the c/a values of the comparative example and Example 1 at different calcination temperatures.

是本对比例与实施例1在不同煅烧温度下的c/a的值。

[n0049]

In the above experimental results, for Example 1, it can be seen from the XRD pattern in Figure 1 that as the calcination temperature increases, the peak splitting degree in the range of 44° -46° increases, indicating that the tetragonality of Ba_{0.9}Ca_{0.1}TiO₃ increases with the increase of calcination temperature; it can be seen from the SEM image in Figure 2 that the particles are square, the particle surface is relatively smooth and round, and the particle size increases with the increase of calcination temperature.

上述实验结果中，对于实施例1，从图1的XRD图中可以看出，随着煅烧温度提高，44°-46°的范围内的峰劈裂程度增强，说明Ba_{0.9}Ca_{0.1}TiO₃的四方性随煅烧温度提高而增加；从图2的SEM图中可以看出，颗粒呈方形，颗粒表面较为光滑圆润，且随着煅烧温度提高，颗粒大小随之增加。

[n0050]

For Example 2, it can be seen from the XRD pattern in Figure 3 that the peak splitting degree in the range of 44°-46° increases with the increase of calcination temperature, indicating that the tetragonality of Ba_{0.8}Ca_{0.2}TiO₃ increases with the increase of calcination temperature, while the splitting degree is the same at 1000°C and 1100°C; it can be seen from the SEM pattern in Figure 4 that at 1000°C, the particles are square and the particle surface is relatively smooth and round, but at 1100°C, there are no obvious grain boundaries between particles, indicating that it is about to be over-calcined.

对于实施例2，从图3的XRD图中可以看出，随着煅烧温度提高，44°-46°的范围内的峰劈裂程度增强，说明Ba_{0.8}Ca_{0.2}TiO₃的四方性随煅烧温度提高而增加，而1000℃与1100℃时的劈裂程度一样；从图4的SEM图中可以看出，在1000℃时，颗粒呈方形，颗粒表面较为光滑圆润，但是在1100℃时，无明显的颗粒与颗粒之间的晶界，即将过烧。

[n0051]

Table 1. c/a values and dielectric constants of barium titanate powders at different calcination temperatures in the examples and comparative examples.

表1 实施例和对比例在不同煅烧温度下的钛酸钡粉体的c/a值、介电常数。

[n0053]

Table 1 shows that the atmospheric pressure hydrothermal assisted solid-state process can prepare barium titanate with high tetragonality. When a small amount of Ca is doped, the tetragonality of barium titanate is significantly improved. When Ba_{0.8}Ca_{0.2}TiO₃ is calcined at 1000℃, c/a = 1.01, and when Ba_{0.9}Ca_{0.1}TiO₃ is calcined at 1100℃, c/a = 1.011. At the same calcination temperature, Ba_{0.8}Ca_{0.2}TiO₃ has higher tetragonality. Therefore, the calcination temperature is closely related to the amount of Ca doping. When performing A-site Ca doping on BaTiO₃, the required calcination temperature decreases as the amount of Ca increases.

从表1中看出，采用常压水热辅助固相法的工艺可制备出高四方性的钛酸钡基，在掺杂少量Ca元素时，较大程度地提高了钛酸钡基的四方性，Ba_{0.8}Ca_{0.2}TiO₃在1000°C煅烧时，c/a＝1.01，Ba_{0.9}Ca_{0.1}TiO₃在1100°C煅烧时，c/a＝1.011，在同样的煅烧温度下，Ba_{0.8}Ca_{0.2}TiO₃的四方性更高，因此煅烧温度与Ca的掺杂量有很大的关系，在对BaTiO₃进行A位的Ca掺杂时，随着掺杂量的增多，所需的煅烧温度降低。

The dielectric constant is usually positively correlated with the tetragonal c/a value. The BaTiO₃ and calcium-doped barium carbonate (BCT) materials prepared under the above conditions have a much larger dielectric constant than BaTiO₃ when the Ca doping amount is 0.2. The former is more than twice that of the latter.

介电常数通常与四方性c/a值的大小正相关，通过上述条件下制备的BaTiO₃和钙掺杂碳酸钡(BCT)材料，Ca元素掺杂量为0.2时的BCT，其介电常数远大于BaTiO₃，前者比后者的2倍还多。

[n0054]

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。