Notice

DESCRIPTION CN114853468A

A high-dielectric- and low-loss doped barium calcium titanate ceramic and its preparation method

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一种高介电低损耗掺杂钛酸钡钙陶瓷及其制备方法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to the field of inorganic non-metallic material preparation, specifically to the field of ferroelectric ceramic materials technology. It provides a high-dielectric-strength, low-loss doped barium calcium titanate ceramic and its preparation method. The method employs a traditional solid-state reaction method to prepare a lead-free, non-volatile, and non-toxic barium calcium titanate modified ceramic with high dielectric strength and low loss. Specifically, it is a low-temperature sintered Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramic, suitable for preparing high-energy-density memory and large-capacity capacitors. Its preparation process is simple, low-cost, and environmentally friendly, aligning with the development direction of dielectric materials. Compared with currently used lead-based, BiFeO₃based, and Bi_{0.5}Na_{0.5}TiO₃based dielectric ceramics, it has higher industrial application value.

本发明涉及无机非金属材料制备领域，具体涉及铁电陶瓷材料技术领域，提供一种高介电低损耗掺杂钛酸钡钙陶瓷及其制备方法，采用传统的固相反应法制备得到无铅、无挥发性且无毒元素的高介电低损耗的钛酸钡钙改性陶瓷，具体是一种低温烧结Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷，适合于制备

高能量密度存储器和大容量电容器，其制备工艺简单、成本低廉、绿色环保，符合介电材料的发展方向，与目前实用铅基、BiFeO₃基和Bi_{0.5}Na_{0.5}TiO₃基介电陶瓷相比，具有较高的工业应用价值。

[0003]

Background Technology

背景技术

[n0002]

The rapid development of the economy and technology, the control of toxic elements by the WEEE Act and RoHS Act, and the strategic need for sustainable development have led to higher requirements for the electrical performance and environmental protection of ceramic application devices. For example, high energy density memory and large capacity capacitors require dielectric materials to have both high dielectric constant, low dielectric loss and good dielectric thermal stability.

经济和科技的高速发展、WEEE法案和RoHS法案对有毒元素物质的管控以及可持续发展的战略需求，市场对陶瓷应用器件的电性能和环保性提出了更高的要求，如高能量密度存储器和大容量电容器要求介电材料兼具高介电常数、低介电损耗和良好的介电热稳定性。

Currently, research on lead-free dielectric ceramics is mostly focused on high Curie point lead-free ceramics such as BiFeO₃based, Bi_{0.5}Na_{0.5}TiO₃based ceramics. However, the high-temperature volatility of Bi and Na pollutes the environment, so the development of environmentally friendly lead-free ceramics with high dielectric properties has important industrial application value.

目前，无铅介电陶瓷的研究热点多集中于高居里点无铅陶瓷如BiFeO₃基、Bi_{0.5}Na_{0.5}TiO₃基陶瓷，但Bi和Na的高温挥发性污染环境，环境友好型高介电性能无铅陶瓷的研发具有重要的工业应用价值。

In recent years, BaTiO4-based lead-free ceramics have become important candidate materials for applications such as filters, resonators, sensors, high-energy-density memories, and capacitors due to their high chemical stability, excellent dielectric properties, and tunable piezoelectricity. However, their room-temperature relative permittivity ε_r is usually below 4000, ε_r varies greatly near their polycrystalline phase transition point, their dielectric properties have poor temperature stability, and their sintering temperature T_s is relatively high (>1350°C). These shortcomings limit their applications.

近年来，BaTiO₃基无铅陶瓷以其高化学稳定性、优异的介电性能和压电性可调成为滤波器、谐振器、传感器、高能量密度存储器和电容器应用的重要候选材料，然而其室温相对介电常数ε_r通常低于4000，在其多晶相转变点附近ε_r变化大，介电性的温度稳定性差，烧结温度T_s偏高(>1350°C)，这些缺点限制了其应用。

In practical applications, changes in ambient temperature and the heat dissipated by equipment cause fluctuations in the operating temperature of dielectric materials, resulting in significant changes in their dielectric constant and dielectric loss. This can easily lead to interruptions in the signal transmission of electronic devices. Effectively improving the room temperature dielectric constant, reducing dielectric loss, and enhancing the thermal stability of dielectric properties of BaTiO2-based ceramics is a current technical bottleneck in the research of BaTiO2-based dielectric ceramics.

实际工作中，周围环境温度的变化和设备散发热量的影响导致介电材料的工作温度发生波动，其介电常数和介电损耗随之发生巨大变化容易导致电子器件工作信号传输中断，如何有效的提高BaTiO₃基陶瓷的室温介电常数、降低介电损耗和改善介电性的热稳定性，是目前BaTiO₃基介电陶瓷研究中的一个技术瓶颈。

[0005]

Summary of the Invention

发明内容

[n0003]

To address the technical problem that BaTiO2-based lead-free ceramics cannot simultaneously achieve high dielectric constant, low loss, good thermal stability, and high temperature stability, this invention provides a doped barium calcium titanate ceramic with high dielectric constant, low loss, and high temperature stability, and its preparation method. The BaTiO24CaTiO25TiTiO26(NbTiO27FeTiO28)TiO30 ceramic prepared using this method exhibits a high εNER31 value (up to 4869) at room temperature, a dielectric loss (tanδ) below 0.037, and good dielectric constant stability from room temperature to 200°C (the rate of change of dielectric constant with temperature, ΔεNER32/εNER33, is <35%).

针对上述BaTiO₃基无铅陶瓷无法兼顾高介电、低损耗、良好的热稳定性和T_s偏高的技术问题，本发明提供一种高介电常数、低损耗、高温度稳定性的掺杂钛酸钡钙陶瓷及其制备方法，利用该方法制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷在室温下ε_r高达4869，介电损耗tanδ低于0.037，室温～200°C其介电常数稳定性良好(介电常数随着温度的变化率△ε_r/ε_r<35%)。

[n0004]

This invention provides a high dielectric and low loss doped barium calcium titanate ceramic with the chemical formula Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃, where x is the number of moles of (Nb_{0.5}Fe_{0.5})⁴⁺ doped in the compound, and 0.04≤x≤0.06.

本发明提供一种高介电低损耗掺杂钛酸钡钙陶瓷，其化学式为Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃，其中x为化合物中掺杂(Nb_{0.5}Fe_{0.5})⁴⁺的摩尔数，0.04≤x≤0.06。

[n0005]

The above-mentioned method for preparing high-dielectric- and low-loss doped barium calcium titanate ceramics is carried out according to the following steps:

上述一种高介电低损耗掺杂钛酸钡钙陶瓷的制备方法，按以下步骤进行：

[n0006]

(1) Analytical grade BaCO, CaCO, TiO, FeO, and MnO powders and 98% purity MnO powder were weighed according to the stoichiometric ratio of the chemical formulas BaCO, CaCO,

TiO, FeO, and MnO powders. Where 0.04≤x≤0.06; the powder is mixed with anhydrous ethanol medium, and wet-milled for 20-24 hours using a planetary ball mill at a speed of 150-175 rpm with agate grinding balls as the grinding medium. The mixture is homogeneous, and the mass ratio of anhydrous ethanol medium to the total mass of powder is (1.1-1.5):1. The grinding balls used are composed of agate balls with diameters of 20mm, 10mm and 6mm in a number ratio of 1:11:16. The slurry is then dried.

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(1)按化学式Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃的化学计量比称量分析纯级别的BaCO₃、CaCO₃、TiO₂、Fe₂O₃粉料和98%纯度的MnO₂粉料，其中0.04≤x≤0.06；将粉料加入无水乙醇媒质混合，以玛瑙磨球为球磨介质用行星式球磨机以150～175转/min的转速用湿法球磨20～24h混合均匀，其中无水乙醇媒质的质量与粉料总质量的配比为(1.1～1.5):1；所用磨球由直径为20mm、10mm和6mm的玛瑙球按个数比1:11:16组成，然后烘干浆料；

[n0007]

(2) Add 5-8 wt% deionized water to the obtained powder according to the weight of the raw materials, press it into blocks at 9-11 MPa for 1-2 min using a tablet press, heat it to 900-930°C at a rate of 3-5°C/min and hold it for 3-4 h for pre-sintering, and cool it to room temperature with the furnace to obtain pre-sintered tablets.

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(2)所得粉料按所述原料的重量加入5～8wt%的去离子水，用压片机在9～11MPa保压1～2min进行压块，以3～5℃/min的速度升温至900～930℃时保温3～4h进行预烧，随炉冷却至室温，得到预烧结压片；

[n0008]

(3) The pre-sintered compressed tablets are pulverized and ball-milled at a speed of 150-175 rpm for 20-24 hours using a wet ball milling process. The mixture is then dried in a drying oven. A polyvinyl alcohol solution binder with a mass concentration of 6-8% is added. The amount of binder added is 3% of the mass of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO_NER63 powder. ~6%, then aged for 22-24 hours, granulated, sieved, and pressed into thin round preforms at 4-7 MPa for 1-3 minutes using a tablet press. The preforms were then buried with powder of the same composition, heated to 600°C at a rate of 3-5°C/min, held for 2 hours to remove the plastic, and cooled to room temperature in the furnace to obtain Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ preforms.

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(3)将预烧结压片粉碎，采用湿法球磨工艺以150～175转/min的转速球磨20～24h混合均匀，置于干燥箱中烘干，加入质量浓度为6～8%的聚乙烯醇溶液粘合剂，所述粘结剂的加入量为Ba<sub>0.70<

/sub>Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃粉体质量的3～6%，然后陈化22～24h，造粒，过筛，用压片机在4～7MPa保持1～3min压成薄圆片胚体，用相同组分粉料掩埋，以3～5°C/min速度升温至600°C时保温2h排塑，随炉冷却至室温得到Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃胚体；

[n0009]

(4) The Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ preforms were sintered in an air atmosphere using a three-stage stepped heating method: the temperature was increased to 600°C at a rate of 2-4°C/min and held for 2h, then increased to 900°C at a rate of 1.5-3°C/min and held for 2h, and finally increased to 1230-1300°C at a rate of 1-2°C/min and held for 4-5h. The preforms were then cooled to room temperature in the furnace to obtain barium calcium titanate ceramic preforms.

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(4)采用三段式阶梯升温的方法将Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃胚体在空气氛围中烧结：以2～4°C/min的速度升温至600°C时保温2h，再以1.5～3°C/min速度升温至900°C时保温2h，最后以1～2°C/min的速度升温至1230～1300°C时保温4～5h烧结，随炉冷却至室温获得掺杂钛酸钡钙陶瓷胚体；

[n0010]

(5) The obtained barium calcium titanate ceramic is annealed at 950-1000°C and cooled to room temperature in air in the furnace to obtain the high dielectric and low loss doped barium calcium titanate ceramic.

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(5)所得掺杂钛酸钡钙陶瓷在950～1000°C进行退火处理，在空气中随炉冷却至室温，制得所述高介电低损耗掺杂钛酸钡钙陶瓷。

[n0011]

Advantages of this invention:

本发明的优点：

[n0012]

1.

1.

This invention broadens the tetragonal working temperature range of BaTiO₃ ceramics by introducing A-site Ca partial substitution to maintain its T_NER79 essentially

unchanged (~128°C), improves the dielectric temperature stability of BaTiO₃ ceramics, and introduces donor Nb⁵⁺ ions and acceptor Fe³⁺ ions to achieve a coexistence of room-temperature ferroelectric tetragonal phase and dielectric orthorhombic phase in Ba_{0.70}Ca_{0.30}TiO_NER The 85 ceramic was subjected to B-site composite doping. The increase in the concentration of composite ions (Nb_{0.5}Fe_{0.5})⁴⁺ reduced the sintering temperature of the ceramic by 110°C. The prepared Ba_{0.70}Ca_{0.30}Ti_{1-x} (Nb_{0.5}Fe_{0.5})_xO₃ ceramic samples exhibited a perovskite structure with pseudocubic-orthorhombic two-phase coexistence, and the density was higher than 94%.

本发明通过在BaTiO₃陶瓷中引入A位Ca部分取代使其T_C基本不变(～128°C)，拓宽了其四方相工作温区，改善了BaTiO₃陶瓷的介电温度稳定性，并引入施主Nb⁵⁺离子和受主Fe³⁺离子对室温铁电四方相-介电正交相两相共存的Ba_{0.70}Ca_{0.30}TiO₃陶瓷进行B位复合掺杂，复合离子(Nb_{0.5}Fe_{0.5})⁴⁺掺杂浓度的提高将陶瓷的烧结温度降低了110°C，制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品呈赝立方-正交两相共存的钙钛矿结构，致密度均高于94%；

[n0013]

2.

2.

The Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramics prepared by this invention have a room temperature ε_r>4100 and tanδ<0.037, wherein Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_NER1 The 09_O_NER110 ceramic exhibits the best room temperature dielectric properties and dielectric temperature stability, with T_s＝1230℃, ε_r and tanδ being 4869 and 0.037, respectively. In the temperature range of room temperature to 200℃, the rate of change of ε_r with temperature, Δε_r/ε_r, is <35%, indicating significant application potential in the fabrication of high-energy-density memory and large-capacity capacitors.

本发明制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷的室温ε_r>4100，tanδ<0.037，其中Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃陶瓷的室温介电性能和介电温度稳定性

最佳，T_s＝1230℃，ε_r和tanδ分别为4869和0.037，在室温～200℃温度范围内，ε_r随温度的变化率△ε_r/ε_r<35%，在高能量密度存储器和大容量电容器的制备方面具有较大应用潜力；

[n0014]

3.

3.

The ferroelectric-paraelectric phase transition characteristic temperature T_NER123 of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramics prepared in this invention monotonically decreases with increasing (Nb_{0.5}Fe_{0.5})⁴⁺ doping concentration, and T_NER127 decreases from 128°C for undoped Ba_{0.70}Ca_{0.30}Ti ceramics to 45°C for Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃ ceramics. (2.0 mol% (Nb_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramics) Doping with 37FeNER138NER139 results in the best room-temperature ferroelectricity of BaNER140CaNER141TiONER142 ceramics. Excessive doping (x≥0.02) reduces the ferroelectric performance parameters (maximum polarization intensity P_NER143, remanent polarization

intensity P_NER144, and coercive field E_NER145) of the samples. In the composition range of 0.04≤x≤0.06, BaNER146CaNER147TiNER148(Nb_NER149Fe_NER150)NER151ONER152 ceramics exhibit good dielectric temperature stability (Δε_NER153/ε_NER154<35%) in the temperature range of room temperature to 200°C.

本发明制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷的铁电-顺电相变特征温度T_m随着(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量的增大单调减小，T_m由未掺杂Ba_{0.70}Ca_{0.30}Ti陶瓷的128°C降至Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃陶瓷的45°C，2.0mol%(Nb_{0.5}Fe_{0.5})⁴⁺掺杂使Ba_{0.70}Ca_{0.30}TiO₃陶瓷的室温铁电性最佳，过量掺杂(x≥0.02)使样品的铁电性能参数(极化强度最大值P_{max}、剩余极化强度P_r和矫顽场E_C)降低，0.04≤x≤0.06组分范围内Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃陶瓷在室温～200°C温度区间呈现良好的介电温度稳定性(△ε_r/ε_r<35%)。

[n0015]

4.

4.

The high dielectric and low loss doped barium calcium titanate lead-free ceramic obtained by this invention has a simple preparation process, no volatile elements, is green and environmentally friendly, has a sintering temperature below 1300°C, is low in cost, and is easy to mass-produce in industrial applications. It has high dielectric, low loss and good dielectric thermal stability, and has great practical potential in high energy density memory and large capacity capacitor applications.

本发明获得的高介电低损耗掺杂钛酸钡钙无铅陶瓷的制备工艺简单，无挥发性元素，绿色环保，烧结温度低于1300°C，成本低廉，易于工业化批量生产，兼具高介电、低损耗和良好的介电热稳定性，在高能量密度存储器和大容量电容器应用方面具有巨大实用潜力。

[0019]

Attached Figure Description

附图说明

[n0016]

Figure 1 shows the powder X-ray diffraction (XRD) pattern of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO_NER161 ceramic (0≤x≤0.12) prepared according to Specific Embodiment Six; Figure 2 shows the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO_NER16 ceramic prepared according to Specific Embodiment Six. Figure 8 shows surface backscattered electron microscopy (SEM) images of ceramic samples (x = 0.004, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, and 0.12); Figure 3 shows the surface backscattered electron microscopy (SEM) images of Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO_NER175 ceramic samples (x = 0.004, 0.01, 0.02, 0.03, 0.04, 0.0) prepared according to specific embodiment six. The relative permittivity ε_r and dielectric loss tangent tanδ of (5, 0.06, 0.08, and 0.12) are shown as curves of temperature variation. Figure 4 shows the characteristic temperature T_m and the dielectric anomalous peak full width at half maximum (FWHM) of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramic sample prepared in specific embodiment six as a function of temperature (Nb_{0.5}Fe_N Figure 5 shows the dielectric relaxation characteristic analysis curves of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramic samples prepared according to specific embodiment six, including the dielectric relaxation characteristic analysis curves according to the Vogel-Fulcher formula f＝f₀exp[-E_a/k_B(T_m-

[T_f], modified Curie-Weiss law 1/ε_r-1/ε_m＝(T-T_m)γ/C, ΔT_{relax}＝T_{m(100kHz)}-T_{m(1kHz)} fitted and calculated T_m-lnf curve, ln(1/ε_r-1/ε_m)-ln(T-T_m) curve, Vogel-Fulcher freezing temperature T_f -x curves and dielectric relaxation index γ and characteristic temperature variation with frequency ΔT_{relax} as a function of (Nb_{0.5}Fe_{0.5})⁴⁺ doping amount x; Figure 6 shows the room temperature dielectric properties ε_r and tanδ as a function of (N_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramic samples prepared according to specific embodiment six. Figure 7 shows the variation curve of doping amount x for Ba_{0.5}Fe_{0.5})⁴⁺. Figure 7 also shows the room-temperature ferroelectric hysteresis loop (P-) of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ (x＝0, 0.004, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08 and 0.12) ceramic samples prepared according to specific embodiment six. E) and displacement current density-field strength relationship curve (J-E); Figure 8 shows the room temperature ferroelectric performance parameters P_{max}, P_r and E_C of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ ceramic sample prepared in specific embodiment six as a function of the doping amount x of (Nb_{0.5}Fe_{0.5})⁴⁺.

图1为具体实施方式六制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷(0≤x≤0.12)的粉末X射线衍射图谱(XRD)；图2为具体实施方式六制备Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品(x＝0.004,0.01,0.02,0.03,0.04,0.05,0.06,0.08和0.12)的表面背散射扫描电镜照片(SEM)；图3为具体实施方式六制备Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品(x＝0.004,0.01,0.02,0.03,0.04,0.05,0.06,0.08和0.12)的相对介电常数ε_r和介电损耗角正切值tanδ随温度的变化关系曲线；图4为具体实施方式六制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品的特征温度T_m和介电反常峰半高宽(FWHM)随着(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x的变化关系曲线；图5为具体实施方式六制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品的介电弛豫特征分析曲线，包括根据Vogel–Fulcher公式f＝f₀exp[-E_a/k_B(T_m-T_f)]、修正的居里-外斯定律1/ε_r-1/ε_m＝(T-T_m)γ/C、ΔT_{relax}＝T_{m(100kHz)}-T_{m(1kHz)}拟合和计算得到的T_m-lnf曲线、ln(1/ε_r-1/ε_m)-ln(T-T_m)曲线、Vogel-Fulcher冻结温度T_f-x曲线和介电弛豫程度指数γ和特征温度随频率变化量

ΔT_{relax}随(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x的变化关系曲线；图6为具体实施方式六制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品的室温介电性能参数ε_r和tanδ随(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x的变化关系曲线；图7为具体实施方式六制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(x＝0, 0.004,0.01,0.02,0.03,0.04,0.05,0.06,0.08和0.12)陶瓷样品的室温铁电电滞回线(P-E)和位移电流密度-场强关系曲线(J-E)；图8为具体实施方式六制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃陶瓷样品的室温铁电性能参数P_{max}、P_r和E_C随着(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x的变化关系曲线。

[0021]

Detailed Implementation

具体实施方式

[n0017]

The technical solution of the present invention is not limited to the specific embodiments listed below, but also includes any combination of the specific embodiments.

本发明技术方案不局限于以下所列举具体实施方式，还包括各具体实施方式间的任意组合。

[n0018]

Specific Implementation Method 1: The chemical formula of a high dielectric and low loss doped barium calcium titanate ceramic in this implementation method is Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃, where x is the molar ratio of (Nb_{0.5}Fe_{0.5})⁴⁺ in the compound, and 0.04≤x≤0.06.

具体实施方式一：本实施方式一种高介电低损耗掺杂钛酸钡钙陶瓷的化学式为Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃，其中x为化合物中(Nb_{0.5}Fe_{0.5})⁴⁺的摩尔数比，0.04≤x≤0.06。

[n0019]

Specific Implementation Method Two: This implementation method provides a method for preparing high-dielectric- and low-loss doped barium calcium titanate ceramics, which is carried out according to the following steps:

具体实施方式二：本实施方式一种高介电低损耗掺杂钛酸钡钙陶瓷的制备方法，按以下步骤进行：

[n0020]

(1) Analytical purity grade pharmaceutical powders BaCO263, CaCO264, TiO265, Fe266, and MnO267 were weighed according to the stoichiometric ratio of their chemical compositions BaCO263, CaCO264, TiO265, Fe266, and O267, and 98% purity MnO263 was also weighed. 268_Powder, where 0.04≤x≤0.06, the weighed powder is mixed and placed in anhydrous ethanol medium. Using agate grinding balls as the grinding medium, a planetary ball mill is used for wet ball milling at a speed of 150-175 rpm for 20-24 hours to mix evenly. The mass ratio of anhydrous ethanol medium to the total mass of powder is (1.1-1.5):1. The grinding balls used are composed of agate balls with diameters of 20mm, 10mm and 6mm in a number ratio of 1:11:16. The slurry is dried.

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(1)按化学组成Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃的化学计量比称量分析纯级别的药品粉料BaCO₃、CaCO₃、TiO₂、Fe₂O₃和98%纯度的MnO₂粉料，其中0.04≤x≤0.06，将称量得到的粉料混合，放入无水乙醇媒质，以玛瑙磨球为球磨介质用行星式球磨机以150～175转/min的转速湿法球磨20～24h混合均匀，其中无水乙醇媒质的质量与粉料总质量的配比为(1.1～1.5):1；所用磨球由直径为20mm、10mm和6mm的玛瑙球按个数比1:11:16组成，烘干浆料；

[n0021]

(2) Add 5-8 wt% deionized water to the obtained powder according to the weight of the raw materials, press it into blocks at 9-11 MPa for 1-2 min using a tablet press, raise the temperature to 900-930°C at a heating rate of 3-5°C/min and hold for 3-4 h for pre-firing, and cool it to room temperature with the furnace to obtain a pre-sintered preform.

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(2)将所得粉料按所述原料的重量加入5～8wt%的去离子水，用压片机在9～11MPa保压1～2min进行压块，以3～5°C/min的升温速率升至900～930°C保温3～4h预烧，随炉冷却至室温，得到预烧结胚体；

[n0022]

(3) The pre-sintered green body is crushed and ball-milled at 150-175 rpm for 20-24 hours using anhydrous ethanol as the medium. The mixture is then dried in a drying oven. A 6-8% polyvinyl alcohol solution binder is added. The amount of binder added is Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃powder. The amount of 3-6% is aged in air for 22-24 hours, granulated by sieving through 100 mesh and 150 mesh, and the 150 mesh powder is pressed into thin round blanks at 4-7 MPa for 1-3 minutes. The blanks are buried with powder of the same

composition, held at 600°C for 2 hours to remove the plastic, and cooled to room temperature in the furnace to obtain Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ blanks to be sintered.

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(3)将预烧结胚体粉碎，采用湿法球磨工艺以无水乙醇为媒质以150～175转/min的转速球磨20～24h混合均匀，将浆料置于干燥箱烘干，加入质量浓度为6～8%的聚乙烯醇溶液粘合剂，粘结剂的加入量为Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃粉体质量的3～6%，空气中陈化22～24h，过筛100目和150目造粒，取150目粉料，在4～7MPa保持1～3min压成薄圆片胚体，用相同组分粉料掩埋，在600°C保温2h排塑，随炉冷却至室温，得到Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃待烧结胚体；

[n0023]

(4) Stack the obtained Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ blanks to be sintered, cover them with powder of the same composition, and sinter them in air using a three-stage stepped heating method: heat up to 600°C at a rate of 2-4°C/min and hold for 2h, heat up to 900°C at a rate of 1.5-3°C/min and hold for 2h, and finally heat up to 1230-1340°C at a rate of 1-2°C/min and hold

for 4-5h. Cool to room temperature in the furnace to obtain barium calcium titanate ceramics. The temperature nodes of the three-stage stepped heating method in step (4) are 600°C, 900°C and 1230-1340°C respectively.

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(4)将所得的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃待烧结胚体叠放，用相同组分粉料掩埋，采用三段式阶梯升温的方法在空气中烧结：以2～4°C/min的速度升温至600°C时保温2h，以1.5～3°C/min速率升温至900°C时保温2h，最后以1～2°C/min的速率升温至1230～1340°C时保温4～5h烧结，随炉冷却至室温获得掺杂钛酸钡钙陶瓷，步骤(4)中所述三段式阶梯升温方法的温度节点分别是600°C、900°C和1230～1340°C。

[n0024]

(5) The obtained barium calcium titanate doped ceramic is heated to 950-1000°C at a rate of 1.5-3°C/min and held for 2-3 hours for annealing treatment. It is then cooled to room temperature in the furnace to obtain the high dielectric and low loss doped barium calcium titanate ceramic.

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(5)将所得掺杂钛酸钡钙陶瓷以1.5～3°C/min的速度升温至950～1000°C时保温2～3h进行退火处理、随炉冷却至室温，制得所述高介电低损耗掺杂钛酸钡钙陶瓷。

[n0025]

Specific implementation method three: The difference between this implementation method and specific implementation method two is that in step (1), x = 0.06 and x = 0.08.

具体实施方式三：本实施方式与具体实施方式二不同的是：步骤(1)中x＝0.06，x＝0.08。

Everything else is the same as in Specific Implementation Method Two.

其它与具体实施方式二相同。

[n0026]

Specific implementation method four: This implementation method differs from specific implementation methods two or three in that: the heating rate of the pre-sintered embryo in step (2) is 2-3°C/min, and the pre-sintering condition is 950°C for 4 hours.

具体实施方式四：本实施方式与具体实施方式二或三不同的是：步骤(2)中预烧结胚体的升温速率为2～3℃/min，预烧条件为950℃保温4h。

The rest is the same as in specific implementation method two or three.

其它与具体实施方式二或三相同。

[n0027]

Specific implementation method five: This implementation method differs from one of the specific implementation methods three to four in that the sintering parameters in step (4) are 1230°C and held for 4 hours.

具体实施方式五：本实施方式与具体实施方式三至四之一不同的是：步骤(4)中烧结参数为1230°C保温4h。

The rest is the same as in one of the specific implementation methods three to four.

其它与具体实施方式三至四之一相同。

[n0028]

Specific Implementation Method Six: A method for preparing a high-dielectric- and low-loss doped barium calcium titanate ceramic according to this embodiment is carried out according to the following steps:

具体实施方式六：本实施方式的一种高介电低损耗掺杂钛酸钡钙陶瓷的制备方法，按以下步骤进行：

[n0029]

(1) BaCO297, CaCO298, TiO299, and Fe300ONER301 powders of analytical purity were weighed according to the stoichiometric ratio of their chemical compositions (Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃). The raw material and 98% pure MnO_NER3O2_ powder were mixed in anhydrous ethanol medium and wet-milled for 24 hours at 150 rpm using a planetary ball mill with agate grinding balls as the grinding medium. The mixture was dried and the slurry was dried. The ratio of ethanol mass to total powder mass was (1.1~1.5):1. The grinding balls used were composed of agate balls with diameters of 20 mm, 10 mm and 6 mm in a number ratio of 1:11:16.

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(1)按化学组成Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃的化学计量比称量分析纯级别的BaCO₃、CaCO₃、TiO₂、Fe₂O₃粉料和98%纯度的MnO₂粉料，将粉料放入无水乙醇媒质混合，以玛瑙磨球为球

磨介质用行星式球磨机以150转/min的转速湿法球磨24h混合均匀，烘干浆料，其中酒精质量与粉料总质量的配比为(1.1～1.5):1；所用磨球由直径为20mm、10mm和6mm的玛瑙球按个数比1:11:16组成；

[n0030]

(2) Add 5-8 wt% deionized water to the obtained powder according to the weight of the raw material, press it into blocks at 9 MPa for 2 min using a tablet press, raise it to 900°C at a rate of 4°C/min and hold it for 4 h for pre-firing, and cool it to room temperature with the furnace to obtain a pre-sintered preform.

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(2)将所得粉料按所述原料的重量加入5～8wt%的去离子水，用压片机在9MPa保压2min进行压块，以4°C/min的速率升至900°C保温4h预烧，随炉冷却至室温，得到预烧结胚体；

[n0031]

(3) The pre-sintered green body prepared in step (2) is crushed and ball-milled at 150 rpm for 24 hours using anhydrous ethanol as the medium to mix evenly. The slurry is dried and a polyvinyl alcohol solution binder with a mass concentration of 8% is added. The amount of binder added is Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ powder. 6% by mass, aged in air for 24 hours, granulated by sieving through 100 mesh and 150 mesh, take the 150 mesh powder,

press into thin round blanks at 6 MPa for 1 minute, cover with powder of the same composition, hold at 600°C for 2 hours to remove plastic, cool to room temperature in the furnace to obtain Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ blanks to be sintered;

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(3)将步骤(2)制备的预烧结胚体粉碎，用湿法球磨工艺以无水乙醇为媒质以150转/min的转速球磨24h混合均匀，将浆料烘干，加入质量浓度为8%的聚乙烯醇溶液粘合剂，粘结剂的加入量为Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃粉体质量的6%，空气中陈化24h，过筛100目和150目造粒，取150目粉料，在6MPa保持1min压成薄圆片胚体，用同组分粉料掩埋，在600°C保温2h排塑，随炉冷却至室温，得到Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃待烧结胚体；

[n0032]

(4) Stack the obtained Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ blanks to be sintered, cover them with powder of the same composition, and sinter them in air using a three-stage step heating method: heat up to 600°C at a rate of 3°C/min and hold for 2h, heat up to 900°C at a rate of 2°C

/min and hold for 2h, and finally heat up to 1230°C at a rate of 1°C/min and hold for 4h for sintering. Cool to room temperature with the furnace to obtain barium calcium titanate ceramic.

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(4)将所得的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃待烧结胚体叠放，用相同组分粉料掩埋，采用三段式阶梯升温的方法在空气中烧结：以3°C/min的速度升温至600°C时保温2h，以2°C/min速度升温至900°C时保温2h，最后以1°C/min的速度升温至1230°C时保温4h进行烧结，随炉冷却至室温获得掺杂钛酸钡钙陶瓷。

[n0033]

(5) The obtained barium calcium titanate doped ceramic was heated to 1000°C at a rate of 2°C /min and held for 3h for annealing treatment. It was then cooled to room temperature in the furnace to obtain the high dielectric and low loss doped barium calcium titanate ceramic.

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(5)将所得掺杂钛酸钡钙陶瓷以2°C/min的速度升温至1000°C时保温3h进行退火处理，随炉冷却至室温，制得所述高介电低损耗掺杂钛酸钡钙陶瓷。

[n0034]

In addition, in the chemical formula Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃, x was taken as 0, 0.004, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08 and 0.12 respectively, and experiments were conducted according to the method of this embodiment.

另外，化学式Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃中x分别取0、0.004、0.01、0.02、0.03、0.04、0.05、0.06、0.08和0.12，按照本实施方式的方法进行实验。

[n0035]

The room-temperature XRD pattern of a high-dielectric- and low-loss doped barium calcium titanate ceramic prepared in this embodiment is shown in Figure 1. The single peak (121) near 2θ = 33° and the split peak (002)/(200) near 2θ = 45° indicate that the Ba_{NER332}Ca_{NER333}Ti_{NER334}(Nb_{NER335}Fe_{NER336})_{NER337}O_{NER338} (0≤x≤0.04) sample exhibits a composite perovskite crystal structure with the coexistence of ferroelectric tetragonal (T) and dielectric orthorhombic (O) phases. As the doping concentration x increases, the substitution of B-site Ti_{NER341} by Fe_{NER339} and Nb_{NER340} ions with larger ionic radii leads to the expansion of the sample's unit cell volume, suppressing the tetragonal phase structure. The double peaks near 2θ = 22°, 46°, 52°, and 57° are observed. The peaks

merge into a single peak near x = 0.05 as the doping concentration x increases, indicating that the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.05≤x≤0.08) sample has a pseudocubic (PC)-orthorhombic (O) two-phase coexistence structure. In the XRD pattern, 2θ = 22°, 4 The sharp, narrow single peaks near 6°, 52°, and 57°, along with subsequent dielectric spectroscopy and ferroelectric hysteresis loop analysis, indicate that the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.08<x≤0.12) sample is a composite structure with cubic (C) and orthorhombic (O) phases coexisting.

本实施方式制备一种高介电低损耗掺杂钛酸钡钙陶瓷的室温XRD图谱如图1所示，2θ＝33[°]附近的单峰(121)和2θ＝45°附近的(002)/(200)劈裂峰表明Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0≤x≤0.04)样品呈铁电四方相(T)和介电正交相(O)两相共存的复合钙钛矿晶体结构，随着掺杂量x增大，较大离子半径的Fe³⁺和Nb⁵⁺取代B位Ti⁴⁺导致样品的晶胞体积膨胀，四方相结构被压制，2θ＝22°、46°、52°和57°附近的双峰均随着掺杂量x的增大在x＝0.05附近合并为单峰，表明Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.05≤x≤0.08)样品为赝立方(PC)-正交(O)两相共存结构，XRD图谱中2θ＝22°、46°、52°和57°附近的尖锐、狭窄单峰以及后续的介温谱和铁电电滞回线测试分析表明Ba_{0.70}Ca_{0.30}Ti_{1-x}

(Nb_{0.5}Fe_{0.5})_xO₃(0.08<x≤0.12)样品为立方(C)-正交(O)两相共存的复合结构。

[n0036]

Figure 2 shows the surface backscattered SEM image of the ceramic sample with the chemical formula Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.004≤x≤0.12). B-site composite substitution reduced the sintering temperature of the sample by 110°C. SEM test results show that the ceramic prepared in this embodiment has good crystallinity, full grains, clear grain boundaries, and dense structure. All samples include two grains of different sizes. The larger tetragonal phase (white) grains are dispersed among the smaller orthorhombic phase (black) grains, which is consistent with the XRD test results.

化学式Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.004≤x≤0.12)陶瓷样品的表面背散射SEM照片如图2所示；B位复合取代将样品烧结温度降低了110°C，SEM测试结果表明本实施方式制备的陶瓷结晶良好，晶粒饱满，晶界清晰，结构致密，所有样品均包括两种大小不同的晶粒，四方相(白色)较大晶粒分散的分布在正交相(黑色)小晶粒之间，与XRD测试结果吻合。

Furthermore, the average grain size of both the orthorhombic and tetragonal phases first increases and then decreases with increasing doping concentration.

且正交相和四方相平均晶粒尺寸均随着掺杂量增大先增大后减小。

[n0037]

The upper and lower surfaces of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.004≤x≤0.12) ceramic sample were coated with silver electrodes. The samples were then fired at 600°C for 1 hour to achieve full electrode coverage. The electrode dimensions were 10–13 mm in diameter. An Agilent 4284A impedance analyzer and temperature control device were used to collect data on the unpolarized Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_N) ceramic sample prepared in this embodiment within a temperature range of -90 to 200°C. Figure 3 shows the dielectric thermograms of the ceramic samples (0.004≤x≤0.12) at frequencies of 1kHz, 10kHz, and 100kHz. Figure 4 shows the phase transition temperature T_m and the full width at half maximum (FWHM) of the dielectric anomalous peak as a function of the doping amount x (Nb_{0.5}Fe_{0.5})⁴⁺. It can be seen from the figure that all samples exhibit a dielectric anomalous peak in the temperature range of -90 to 200°C, corresponding to the characteristic temperature T_{0.5}Fe_{0.5}</sub>NER375_O₃(0.004≤x≤0.12). The NER381 and a small amount of (NbNER382FeNER383)NER384 doped samples (0<x≤0.04) exhibit sharp dielectric anomalous peaks. Their εNER385 and tanδ dopants do not change with the test frequency f, indicating no

frequency dispersion or dispersion phase transition. This suggests that the BaNER386CaNER387TiNER388(NbNER389FeNER390)NER391ONER392 (0≤x≤0.04) ceramics are normal ferroelectrics, and their TNER393 decreases monotonically with increasing x. The increase of doping amount x (x≥0.05) in the Nb_{0.5}Fe_{0.5})⁴⁺ strengthens the dielectric relaxation of the ceramic sample, and the T_m monotonically decreases below room temperature. The dielectric anomalous peak gradually broadens and flattens, changing from a sharp peak to a relatively gentle "bump". The full width at half maximum (FWHM) of the peak gradually increases, and FWHM increases sharply near x＝0.05. As the test frequency f increases, its ε_r gradually decreases. The dielectric anomalous peak shifts towards higher temperatures. That is, the frequency dispersion and dispersion phase transition characteristics indicate that the 0.05≤x≤0.12 sample transforms into a relaxor ferroelectric.

将Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.004≤x≤0.12)陶瓷样品的上下表面被覆银电极，在600℃保温1h烧制满电极，电极尺寸为直径10～13mm，采用安捷伦4284A型号阻抗分析仪和温控装置在-90～200℃温度区间采集本实施方式制备的未极化Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.004≤x≤0.12)陶瓷样品在频率为1kHz,10kHz和100kHz的介温谱图如图3所示，获得样品的相变温度T_m和介电反常峰的半高宽(FWHM)随(Nb_{0.5}Fe_{0.5})

⁴⁺掺杂量x的变化曲线如图4所示，从图中可知，在-90～200℃温度范围所有样品均呈现一个介电反常峰，对应于铁电-顺电相变特征温度T_m，少量(Nb_{0.5}Fe_{0.5})⁴⁺掺杂(0<x≤0.04)样品呈现尖锐的介电反常峰，其ε_r和tanδ不随测试频率f改变，即无频率色散和弥散相变现象，表明Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0≤x≤0.04)陶瓷为正常铁电体，其T_m随x增大单调降低；(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x增大(x≥0.05)使陶瓷样品的介电弛豫程度加强，T_m单调降至室温以下，介电反常峰逐渐变宽和平缓，由尖锐的峰转变为较为平缓的“鼓包”，峰的半高宽FWHM逐渐增大，FWHM在x＝0.05附近陡增，随测试频率f增大，其ε_r逐渐减小，介电反常峰向高温方向移动，即频率色散和弥散相变特征表明0.05≤x≤0.12样品转变为弛豫型铁电体。

[n0038]

The dielectric relaxation characteristics of the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ (0≤x≤0.12) ceramic sample prepared in this embodiment were analyzed in detail. Specifically, the dielectric relaxation characteristic analysis curve was obtained by fitting the dielectric spectrum 3, as shown in Figure 5. This includes the analysis based on the Vogel-Fulcher formula f＝f₀exp[-E_a/k_B(T_m-T_f)] and the modified Curie-Weiss law 1/ The curves obtained by fitting and calculating ε_r-1/ε_m＝(T-T_m)γ/C, ΔT<sub>relax<

/sub>＝T_{m(100kHz)}-T_{m(1kHz)}, T_m-lnf curve, ln(1/ε_r-1/ε_m)-ln(T-T_m) curve, Vogel-Fulcher freezing temperature T_f-x curve, and the curves showing the relationship between the dielectric relaxation index γ and the change in frequency f ΔT_{relax} as a function of the composition; it can be seen from the figures that the sample The Vogel-Fulcher freezing temperature T_f decreases monotonically with increasing x, and drops sharply near x = 0.05, indicating that the sample has transformed into a relaxor ferroelectric at this point. Especially at x = 0.06, T_f drops to 41°C, close to room temperature, indicating that the 6 mol% B-site (Nb_{0.5}Fe_{0.5})⁴⁺ doping in Ba_{0.70}Ca_{0.30}TiO₃ transforms it from an ergodic relaxor phase to an ergodic relaxor phase. The relaxation index γ and ΔT_{relax} as a function of composition in Figure 5 show that (Nb_NER43... Increasing the doping amount x of 3_Fe_{0.5})⁴⁺ causes γ and ΔT_{relax} to increase monotonically. The γ values at x = 0.06, 0.08 and 0.12 are 1.67, 1.87 and 1.90, respectively, indicating that the Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.06≤x≤0.12) ceramic samples prepared in this embodiment are transformed into relaxor ferroelectrics. The defect dipole effect introduced by composite doping induces the enhancement of the dielectric relaxation degree of the ceramic, which is beneficial to improving its dielectric temperature stability.

对本实施方式制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0≤x≤0.12)陶瓷样品的介温弛豫特征进行深入分析，即对其介温谱图3进行拟合分析得到介电弛豫特征分析曲线如图5所示，即包括根据Vogel–Fulcher公式f＝f₀exp[-E_a/k_B(T_m-T_f)]、修正的居里-外斯定律1/ε_r-1/ε_m＝(T-T_m)γ/C、ΔT_{relax}＝T_{m(100kHz)}-T_{m(1kHz)}拟合和计算得到的T_m-lnf曲线、ln(1/ε_r-1/ε_m)-ln(T-T_m)曲线、Vogel-Fulcher冻结温度T_f-x曲线和介电弛豫程度指数γ和T_m随频率f的变化量ΔT_{relax}随组分的变化关系曲线；从图中可以看出，样品的Vogel-Fulcher冻结温度T_f随x增大单调降低，在x＝0.05附近陡降，表明此时样品已经转变为弛豫型铁电体，尤其在x＝0.06处T_f降至41℃，接近室温，表明Ba_{0.70}Ca_{0.30}TiO₃中6mol%的B位(Nb_{0.5}Fe_{0.5})⁴⁺掺杂使其由非遍历弛豫相转变为遍历弛豫相，图5中弛豫程度指数γ和ΔT_{relax}随组分的变化关系曲线表明(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x增大使γ和ΔT_{relax}单调增大，x＝0.06、0.08和0.12处γ值分别为1.67、1.87和1.90表明本实施方式制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0.06≤x≤0.12)陶瓷样品转变为弛豫型铁电体，复合掺杂引入的缺陷偶极效应诱导陶瓷的介电弛豫程度增强，有利于其介电温度稳定性的提高。

Using the formula [ε_r(T)-ε_r(RT)]/ε_r(RT), the rate of change of ε_r with temperature for Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O_NER453 ceramic samples in the temperature range of room temperature to 200°C is calculated to be <35%, indicating that they have good dielectric thermal stability.

利用公式[ε_r(T)-ε_r(RT)]/ε_r(RT)计算得到Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃陶瓷样品在室温～200°C温度范围的ε_r随温度的变化率Δε_r/ε_r<35%，表明其具有较好的介电热稳定性。

[n0039]

The room temperature ε_{NER464} and tanδ of the Ba_{NER457}Ca_{NER458}Ti_{NER459}(Nb_{NER460}Fe_{NER461})_{NER462}O_{NER463} (0≤x≤0.12) ceramic prepared in this embodiment were measured using an Agilent 4294A impedance analyzer, as shown in Figure 6. The test results show that B-site (Nb_{NER465}Fe_{NER466})_{NER467} doping of less than 6 mol% can significantly improve the performance of Ba_{NER468}Ca_{NER469}TiO_{NER463}. The room-temperature relative permittivity of R470 ceramics, in the composition range of 0.04≤x≤0.06,

is ε_r>4100 and tanδ<0.037. The rate of change of ε_r with temperature, Δε_r/ε_r<35%, may be due to the combined effects of increased B-site (Nb_{0.5}Fe_{0.5})⁴⁺ doping, resulting in suppression of the tetragonal phase structure, grain refinement, reduced oxygen octahedral stability, establishment of internal electric field, and lattice defects.

采用安捷伦4294A型号阻抗分析仪测试本实施方式制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(0≤x≤0.12)陶瓷在1kHz时的室温ε_r和tanδ如图6所示，测试结果表明低于6mol%的B位(Nb_{0.5}Fe_{0.5})⁴⁺掺杂可显著提高Ba_{0.70}Ca_{0.30}TiO₃陶瓷的室温相对介电常数，在0.04≤x≤0.06组分范围内样品的ε_r>4100且tanδ<0.037，ε_r随温度的变化率Δε_r/ε_r<35%，其介电性和弛豫程度的增强和T_m的降低可能来自于B位(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量增大引起的四方相结构的压制、晶粒细化、氧八面体稳定性降低、内电场的建立和晶格结构缺陷的共同作用。

[n0040]

Figure 7 shows the hysteresis loop and displacement current density-field strength (J-E) curves of the samples measured using a TD-88A ferroelectric comprehensive tester at room temperature, 10 Hz, and 50 kV/cm electric field. Figure 8 shows the corresponding room-

temperature ferroelectric performance parameters (maximum polarization intensity P_{max}, remanent polarization intensity P_r, and coercive field E_C) as a function of doping concentration. From the figure, it can be seen that (Nb_{0.5}Fe_{0.5})⁴⁺ Increasing the doping concentration x causes the hysteresis loop of the sample to gradually become "taller" and "fatter," and its displacement current-field strength curve exhibits a sharp peak near the coercive field, indicating that the sample with $0 \leqslant x \leqslant 0.04$ is a normal ferroelectric. The optimal room-temperature ferroelectric performance is obtained at x = 0.02: P_{max} = 12.8 μC /cm², P_r = 6.1 μC/cm², E_C = 6.0 kV/cm. When x increases above 0.05, the hysteresis loop becomes "thinner" and "fatter." The sharp peaks near the coercive field in the J-E curves of samples with $x \leqslant 0.08$ disappeared and became flatter. The maximum position of the Ba_{0.70}Ca<sub>0.30< /sub>Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃ (x＝0,0.004,0.01,0.02,0.03,0.04,0.05,0.06,0.08) ceramic samples prepared in this embodiment was measured during positive cycling. The transfer current densities J_{max} are 0.0103 mA/cm², 0.0176 mA/cm², 0.0216 mA/cm², 0.0290 mA/cm², 0.0161 mA/cm², 0.0164 mA/cm², 0.0102 mA/cm², 0.0069 mA/cm² and 0.0046 mA/cm². The changes in ferroelectricity are consistent with the PC-O multiphase structure and the enhanced relaxation characteristics of the samples. This may be due to the combined effects of grain size effect, the clamping effect of the internal electric field on the domain walls, phase

transition, and lattice structure distortion.

采用TD-88A铁电综合测试仪在室温、10Hz、50kV/cm电场下测样品的电滞回线和位移电流密度-场强关系(J-E)曲线如图7所示，其对应的室温铁电性能参数(极化强度最大值P_{max}、剩余极化强度P_r和矫顽场E_C)随着掺杂量的变化关系如图8所示，从图中可知，(Nb_{0.5}Fe_{0.5})⁴⁺掺杂量x增大使样品的电滞回线逐渐变“高”和“胖”，其位移电流-场强曲线在矫顽场附近呈现尖锐的峰，表明0≤x≤0.04样品为正常铁电体，在x＝0.02处获得最佳室温铁电性能P_{max}＝12.8μC/cm², P_r＝6.1μC/cm²,E_C＝6.0kV/cm，x增大到0.05以上时回线变得“瘦”且“扁平”，0.05≤x≤0.08样品的J-E曲线中矫顽场附近的尖锐峰消失，变得平缓，正循环中测得本实施方式制备的Ba_{0.70}Ca_{0.30}Ti_{1-x}(Nb_{0.5}Fe_{0.5})_xO₃(x＝0, 0.004,0.01,0.02,0.03,0.04,0.05,0.06,0.08)陶瓷样品的最大位移电流密度J_{max}分别为0.0103mA/cm²,0.0176mA/cm²,0.0216mA/cm²,0.0290 mA/cm²,0.0161mA/cm²,0.0164mA/cm²,0.0102mA /cm²,0.0069mA/cm²and 0.0046mA/cm²，其铁电性变化与样品的PC-O复相结构和弛豫特征增强现象相吻合，这可能来自晶粒尺寸效应、内电场对畴壁的夹持效应、相变、晶格结构畸变的共同作用。

[n0041]

As shown in Figures 1 to 8, the Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O_NER513 ceramic samples prepared in this embodiment possess high dielectric constant, low loss, and good temperature stability. Their comprehensive electrical performance parameters are: ε_r＝4869, tanδ＝0.037, T_m＝45°C, P_{max}＝8.0μC/cm², P_r＝1.9μC/cm_NER519 E_C＝3.1kV/cm, the rate of change of relative permittivity with temperature [ε_r(T)-ε_{rm}(RT)]/ε_{rm}(RT)<35%, the Vogel-Fulcher freezing temperature T_f＝41°C, the relaxation index γ＝1.67, its high dielectric constant, low loss, good dielectric thermal stability, T_s below 1300°C, simple preparation process, lead-free and free of volatile elements, indicate that it has high commercial application value in high energy density memory and large capacity capacitor applications.

由图1至图8可知，本实施方式制备的Ba_{0.70}Ca_{0.30}Ti_{0.94}(Nb_{0.5}Fe_{0.5})_{0.06}O₃陶瓷样品兼具高介电、低损耗和良好的温度稳定性，其综合电性能参数为：ε_r＝4869,tanδ＝0.037,T_m＝45°C,P_{max}＝8.0μC/cm²,P_r＝1.9μC/cm²,E_C＝3.1kV/cm,相对介电常数随温度的变化率[ε_r(T)-ε_{rm}(RT)]/ε_{rm}(RT)<35%，Vogel-Fulcher冻结温度T_f＝41°C，弛豫程度指数γ＝1.67，其高介电、低损耗、良好的介电热稳定性、T_s

低于1300°C、制备工艺简单、无铅且无挥发性元素，表明其在高能量密度存储器和大容量电容器应用方面具有较高商业应用价值。