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硕士学位论文

巨电容率CaCu3Ti4O12陶瓷的制备及其晶粒和晶界非线性特性

Preparation of CaCu3Ti4O12 Ceramics with Giant Permittivity and Its Non-Linear I-V Properties in Grains and Grain Boundaries

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摘 要

本论文采用固相法制备CaCu3Ti4O12（简写为CCTO）陶瓷，研究了添加剂含量及成型工艺对CCTO陶瓷致密度、微观结构及电气性能等方面的影响。

首先分别以Na0.5Bi0.5Cu3Ti4O12（简写为NBCTO）、Bi0.667Cu3Ti4O12（简写为BCTO）为单一添加剂，CuO-TiO2-La2O3（简写为Cu/Ti/La）为复合添加剂，采用干压成型法制备CCTO块体陶瓷。实验结果表明：当NBCTO含量为5%时，陶瓷形成具有明显立方晶粒的单一钙钛矿结构CCTO基陶瓷，此时陶瓷的电容率达到最大值ℰr=696770（1kHz），对应的介电损耗为tanδ=0.526，非线性系数和击穿场强分别为2.79和9.01V/mm；CCTO-BCTO体系中，BCTO含量为5%时，样品的致密度达到最大，此时介电损耗达到最小值0.266（1kHz），对应的电容率ℰr=458080，但陶瓷的电容率在BCTO含量为10%时达到最大值ℰr=584007（1kHz），对应的介电损耗为tanδ=0.42；在Cu/Ti/La三掺杂体系中，电容率随添加量的增加而减小，当Cu/Ti/La添加量为4%时，样品的致密度和收缩率达到最大，分别为96.3%和14.02%，此时介电损耗达到最小值0.041（1kHz），对应的电容率ℰr=75862；Cu/Ti/La三掺杂CCTO陶瓷所有样品非线性系数在3~6之间。

其次采用流延成型工艺制备纯CCTO薄片坯体，在不同温度下进行烧结，研究烧结温度对CCTO陶瓷结构和电气性能的影响。流延法制备的CCTO陶瓷在1060~1100℃烧结5h都形成了化学成分单一的CCTO相，晶粒大小分布在100~200μm，其中1080℃烧结5h的薄片陶瓷介电性能最佳，1kHz时ℰr=98606，tanδ=0.0285，同时也具有较好的非线性特征，非线性系数α=5.06，击穿场强为38.2V/mm。

在上述实验基础上，对CCTO介电机理和压敏机理进行初步探讨。通过对流延成型CCTO陶瓷样品的晶粒、晶界成分分析，发现CCTO陶瓷晶粒和晶界的成分存在较大区别，其中晶界处铜元素含量是晶粒内的4倍；CCTO陶瓷中添加10%的BCTO，晶界电阻降低98%，晶粒电阻几乎不变，晶界激活能从纯CCTO的0.741eV降到0.9CCTO-0.1BCTO的0.379eV。对流延成型和干压成型纯CCTO陶瓷的复阻抗分析并且结合电镜照片、光学显微照片发现在CCTO陶瓷多晶体中不仅有晶粒-晶界结构，晶粒内部还

存在着区别于晶界的畴结构。采用光刻工艺在CCTO陶瓷表面制备20μm的方形微电极，利用微探针直接测量晶粒内部和晶界之间的I-V特性曲线，实验结果表明晶界属于高阻区，晶粒内部电阻较晶界电阻低，晶粒内部和晶粒之间都存在明显的势垒。为此，提出改进的内部阻挡层电容模型（IBLC模型）结合双Schottky势垒模型部分解释了CCTO陶瓷材料的巨介电性和压敏性。

最后，利用CCTO陶瓷成功制备了电容-压敏双功能元件。电容器电容量为5.65μF，介电损耗0.061（1kHz），绝缘电阻34.2 KΩ，样品非线性系数5.19，压敏电压10.3V。并搭建电路，对电容器进行了充放电性能测试。

关键词：巨电容率；CCTO陶瓷；双功能

Abstract

In this thesis, Ceramics CaCu3Ti4O12, i.e., CCTO, were prepared by the conventional solid-state reaction. The effects of forming technique and amount of different dopants on chemical structure, dielectric properties and J-E response of the samples were studied.

Firstly, Na0.5Bi0.5Cu3Ti4O12, i.e., NBCTO, and Bi0.667Cu3Ti4O12, i.e., BCTO, were chosen as single additives, respectively, and, CuO-TiO2-La2O3, i.e., Cu/Ti/La, were chosen as multiple additives. CCTO samples were formed by dry-pressure forming. The results showed that a pure perovskite structure for CCTO ceramics was obtained when NBCTO content was 5%. The dielectric constant was 696770 and dielectric loss was 0.526 at 1 kHz, and the nonlinear coefficients and the electric field with standing were 2.79 and 9.01V/mm, respectively. Similar results were obtained by adding BCTO. As additive amount was 5%, the relative density of ceramic was increased into 96.9% with dielectric constant and dielectric loss of 458080 and 0.266 at 1 kHz, respectively. But dielectric constant was reached at the highest value of 584007, when BCTO content was 10%, and dielectric loss was 0.42. In the system of Cu/Ti/La composite additives, with the increasing of Cu/Ti/La concentration, the dielectric constant was decreased, but the dielectric loss firstly was decreased and then increased. Density and shrinkage rate reached the maximum value of 96.3% and 14.02%, respectively, when the content was 4%, dielectric loss had minimum value of 0.041, and dielectric constant was 75862. The nonlinear coefficients of the samples were between 3 and 6.

Through systematical study the different sinter temperature on properties of CCTO ceramics by tape casting, XRD results showed a pure perovskite phase was obtained after heat treatment at 1080 for 5h, and clear grain boundary, higher density, giant dielectric constant and ideal dielectric loss was achieved.

The dielectricconstant was 98606, and the dielectric loss was 0.0285 at 1 kHz. The sample sintered at 1080 for 5h also had good nonlinear characteristics, the breakdown voltage was 38.2V/mm and the nonlinear coefficient was 5.06.
Based on above experimental researches, the CCTO ceramics with nonlinear electric properties and giant dielectric constant, had been prepared for mechanism study in this thesis. Analysis on the grain and the grain boundary composition of the CCTO ceramics formed by tape casting,there are great differences between them, the copper element content is 4 times of the grain boundary to the grain. Addition of 10% BCTO in CCTO ceramics, the grain boundary resistance is reduced by 98%, but the grain resistance is unaltered, the activation energy of grain boundary from 0.741eV of the pure CCTO to 0.379eV of the 0.9CCTO-0.1BCTO. Analysis of CCTO samples formed by the dry pressure forming and tape casting by complex impedance, combined with SEMoptical microscope,was founded that CCTO ceramics not only had grains, but also had domains structure in the grains interior different from grain boundary. Square microelectrode was made on the surface of CCTO ceramics prepared by lithography technics, I-V curves of grains and grain boundaries had direct measured, the experimental results show that the grain boundary belongs to the high resistance region, the grain resistance is smaller than grain boundary resistance. It had obvious barriers in the grain and grain boundary.
Finally, CCTO ceramic multi-layer chip components with twin functions were obtained by using of CCTO ceramics. The capacitance of the sample was 5.65 μF and dielectric loss was 0.061 at 1kHz, and non-linear coefficient and electric field withstanding were 5.19 and 10.3V, respectively. The charge-discharge performance of the sample had also been tested.

Keywords: giant dielectric constant; CCTO ceramics; twin functions

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