学校编码：10384　　密级_____

学号：20720081150596

厦门大学

硕 士 学 位 论 文

双功能陶瓷 $CaCu_3Ti_4O_{12}$ 的制备及其应用

Preparation and Application of $CaCu_3Ti_4O_{12}$ Based Ceramics with Dual-functional Properties

曹 泽 亮

指导教师姓名： 熊兆贤 教授

专 业 名 称： 材 料 学

论文提交日期： 2011 年 6 月

论文答辩时间： 2011 年 月

2011 年 6 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（ 熊兆贤 教授 ）课题（组）的研究成果，获得（ 熊兆贤 教授 ）课题（组）经费或实验室的资助，在（ 熊兆贤 教授 课题组 ）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　　）2.不保密，适用上述授权。

（请在以上相应括号内打“ √”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　　月　　日

摘 要

本论文采用固相法制备 $CaCu_3Ti_4O_{12}$（以下简称 CCTO）粉体，研究了添加剂含量及烧结方法等因素对 CCTO 陶瓷致密度、微观结构及电气性能等方面的影响。

选取 V_2O_5 为单一添加剂，Bi_2O_3-CuO 为复合添加剂，实验结果表明：当 V_2O_5 的添加量为 0.1%时，陶瓷形成一种大小晶粒交错堆叠的致密结构（$\rho_{相对}$=95.97%），CCTO 陶瓷的介电性能表现出较好的频率稳定性和温度稳定性，f=1kHz 时 ε_r=32038 且 tanδ=0.026，CCTO 陶瓷的正反向非线性系数均大于 10；固定 V_2O_5 的添加量，采用两步法烧结有助于提高陶瓷的压敏性能:当 T_2=1020 ℃时，$\rho_{相对}$=97.59%，CCTO 陶瓷的压敏性能较佳，正反向非线性系数均大于 30，但是 CCTO 陶瓷介电性能变差，f=1kHz 时 ε_r=12232 且 tanδ=0.238。添加 Bi_2O_3-CuO 也得到类似的效果，当添加量为 0.5%时，CCTO 陶瓷最致密，$\rho_{相对}$=97.71%, f=1kHz 时 ε_r=62675 且 tanδ=0.086，CCTO 陶瓷的正反向非线性系数均大于 3；采用两步法烧结，当 T_2=1000 ℃时，$\rho_{相对}$ = 95.47%，CCTO 陶瓷压敏性能较佳，正反向非线性系数均大于 55，f=1kHz 时 ε_r=16222 且 tanδ=0.394。

在上述添加剂实验基础上，本论文还进行机理方面的探讨工作，一方面通过熔盐法处理工艺结合两步法烧结在 CCTO 陶瓷体内进行化学处理，制备不同介电常数和压敏性能的 CCTO 陶瓷样品；采用热腐蚀法处理样品的表面和断面，发现晶粒内部存在着区别于晶界的区域——畴界，且阻抗谱分析结果表明：除了晶界和畴界，CCTO 陶瓷样品内部还存在由于缺陷而引起的其它高阻区；另一方面，通过物理方法在 CCTO 陶瓷表面磁控溅射一层不同厚度的 Al_2O_3 绝缘层，实验结果表明：虽然 Al_2O_3 绝缘层的引入使得 CCTO 陶瓷的电容率略有降低，但仍然在 10^4 数量级，且介电损耗变化不大；引入 Al_2O_3 绝缘层使得样品电阻增大，J-E 特性曲线向高场强方向移动，但其非线性系数没有太大变化，这说明 CCTO 陶瓷的巨介电效应和压敏性能都是由于材料体内自身结构引起的。结合上述结论利用双 Schottky 势垒模型，同时引入势垒消失理论，初步解释 CCTO 陶瓷巨介电效应和优异压敏性能的缘由。同时，通过微接触电流-电压测试法测试 CCTO

陶瓷表面不同晶粒和晶界的 I-V 特性曲线验证了上述理论模型的合理性，并且通过简化公式定性地分析了添加剂法和熔盐法的相关实验结果。

最后，利用 CCTO 陶瓷巨介电效应和压敏性能成功地将其开发成外径为 11.31mm 和内径为 6.65mm 的三电极环形压敏电阻器，其厚度为 0.89mm。各电极间介电性能和压敏性能差异较小，在 f=1kHz 时 C>32.92nF 且 tanδ<0.74，正反向非线性系数均大于 2.3 且 E_{10mA}<11.9V。与 TDK 公司 VAR-18 系列产品比较，CCTO 环形压敏电阻器的电气性能与其基本持平，但 CCTO 陶瓷压敏电阻器在制备工艺上的优势，能有效地降低工业化生产成本，有望应用于直流电机的消噪方面。

关键词：双功能陶瓷，CCTO，环形压敏电阻器

Abstract

In this thesis, $CaCu_3Ti_4O_{12}$（CCTO）ceramics were prepared by the conventional solid state reaction. The effects of sintering conditions and amount of different dopants on chemical structure, dielectric properties and J-E response of the sample were studied.

V_2O_5 and Bi_2O_3-CuO were chosen as single and double additives, respectively. The results shown that the large grain was evenly distributed across the small one, and its relative density reached at 95.97%, when V_2O_5 dopant content was 0.1%. The dielectric frequency spectrum indicated good stability over a wide frequency range. The permittivity was almost a constant over the temperature ranges between 5 ℃ and 130 ℃, which exhibited good dielectric-temperature stability. The dielectric constant was 32038 and dielectric loss was 0.026 at 1 kHz, and the forward and reverse nonlinear coefficients were all larger than 10. Fixing the content of V_2O_5, the nonlinear electric properties of CCTO ceramics by the two-step sintering were better than that of the conventional sintering. CCTO ceramics had the highest relatively density (97.59%) sintered at 1120 ℃ for 10min and then 1020 ℃ for 30h, and the forward and reverse nonlinear coefficients were all larger than 30. But its dielectric properties were got worse, the dielectric constant decreased to 12232 and dielectric loss rose to 0.238 at 1 kHz. Similar results were obtained by adding Bi_2O_3-CuO. As additives amount was 0.5%, the relative density of ceramic increased 97.71% with dielectric constant and dielectric loss of 62675 and 0.086 at 1 kHz, respectively. Its forward and reverse nonlinear coefficients were between 3 to 4. By adding Bi_2O_3-CuO and sintered at 1120 ℃ for 10min and then 1000 ℃ for 30h, the relative density of the sample was up to 95.47%. The forward and reverse nonlinear coefficients were all larger than 55, and the dielectric constant was 16222 and dielectric loss was 0.394 at 1 kHz.

Based on above experimental researches, the CCTO ceramics with different dielectric constants and nonlinear electric properties, had been prepared for mechanism study in this thesis. SEM images implied a bump domain boundary

formed inside the grain after thermally etching. According to EIS, in addition to the grain boundary and the domain boundary, there were also some high resistance areas caused by defects. On the other hand, the surfaces of CCTO polycrystalline samples were polished, and deposited different thickness of Al_2O_3 by magneton sputter technology. And then the pellets were coated with Ag paste to form metal electrode. The dielectric constant of those samples was less than that one without treatment, but it was also 10^4 order and its dielectric loss was little changed. The samples with Al_2O_3 insulating layer had larger resistance, and its J-E curve moved to high field strength with similar nonlinear coefficient. These results illustrated that the huge dielectric constant and good nonlinear electric properties were caused by its structure. Combining with the experiment data, the concepts of barrier disappearance were introduced into double Schottky barriers model to explain what CCTO have high dielectric permittivity and good nonlinear electric properties, which were in good agreement with experiment results. Patterned microelectrodes on a polished surface of a specimen, the I–V characteristics were directly measured across different microstructure, and supported the double Schottky barriers model.

In the end of this thesis, CCTO ceramic was developed into ring varistors successfully with dual-functional electric properties, which's internal diameter, outer diameter and thickness were 11.31mm, 6.65mm, 0.89mm respectively. The dielectric property and nonlinear electric property were slightly different between electrodes. The capacitance of the sample was larger than 32.92nF with a dielectric loss smaller than 0.74 at 1 kHz. Meanwhile, its forward and reverse nonlinear coefficients were larger than 2.3, and the breakdown voltage was smaller than 11.90V. Compared with VAR-18 series products made by TDK, the sample had similar electric properties. Owing to the simple preparation, it is decreased the cost of production and can be used in the absorption of noise in DC micro motor.

Keyword: dual-functional ceramics, CCTO, ring varistor

目 录

Contents