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Evolution of $CaCu_3Ti_4O_{12}$ varistor properties during heat treatment in vacuum

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Abstract

Calcium copper titanate ($CaCu_3Ti_4O_{12}$) ceramic varistors were prepared by solid-state method. The samples were several times heat treated in vacuum and the evolution of electrical characteristics were monitored by current density versus electric field measurements and impedance spectroscopy. Repeated heat treatments in vacuum (900 °C for 1 h, 0.01 Torr) lead to a desorption of oxygen adsorbed at the grain boundaries and consequently to a degradation of the varistor properties. During further successive heat treatments some oxygen from the grain interior moves to the grain boundary thereby partially restoring the varistor properties.

Keywords: E. varistors; Calcium copper titanate

1. Introduction

Calcium copper titanate (CCTO) has been studied for the first time in 1967 [1] and has recently attracted strong scientific interest because of its extremely high dielectric constant. From 100 to 600 K, the dielectric constant at 1 kHz is around 10,000 [2], Moreover, when the material is doped with iron(III) on Ti-site, the dielectric constant reaches values up to 150,000 [3]. Chung et al. reported that CCTO exhibits nonlinear current–voltage characteristics even in the absence of any dopants [4]. Atomic force microscopy revealed the presence of an intrinsic electrostatic potential barrier at the grain boundaries that is considered to be responsible for the varistor properties. These outstanding electrical properties are quite unusual since CCTO exhibits a body centered cubic perovskite structure with slightly tilted $[TiO_6]$ octahedra facing each other [5], i.e. the compound is not ferroelectric.

Despite numerous studies including quantum chemical calculations [6], the origin of this high dielectric constant remains still unclear. Impedance spectroscopy has proven that such ceramics consist of semiconducting grains and insulating grain boundaries. Results from Sinclair et al. [7] suggest that the high dielectric constant is actually an internal grain boundary barrier layer capacitance, in other words, it is a grain boundary effect that is not linked to the perovskite crystal structure. Since the nonlinear electrical properties are not independent from the grain boundary nature, one would expect that they are somehow connected to the grain boundary barrier layer capacitance. It is also known that oxygen adsorbed at the grain boundaries plays a fundamental role in the mechanism of a potential barrier formation. The literature contains numerous studies on the influence of heat treatments of varistor ceramics in reducing or oxidizing atmospheres on the electrical properties [8,9]. In the present article, we investigate the role of oxygen adsorbed at the grain boundaries of CCTO varistor ceramics through monitoring their electrical properties during successive heat treatments in vacuum.

2. Experimental procedure

CCTO powder was prepared using the traditional solid-state route similar to a procedure already given by Li et al. [10]. All the oxides used were analytical grade: calcium carbonate (Aldrich, 99.6%), copper(II) oxide (Riedel, 99%) and titanium dioxide (Riedel, 99.8%). Stoichiometric ratios of the educts were ground and mixed by ball milling (30 min) which, however, did not lead

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to mechanochemical activation. The mixture was then calcined at 900 °C for 12 h and afterwards remilled for 30 min. The calcined powder was pressed into pellets by uniaxial pressing (1 MPa) followed by isostatic pressing at 210 MPa. Next, the pellets were sintered in air at 1100 °C for 3 h. The heating and cooling rates were both 5 °C/min.

The X-ray data of the calcined powder were collected with a Rigaku-2000 diffractometer under the following experimental conditions: copper anode, 50 kV, 150 mA, Cu Kα radiation monocromatized by a graphite crystal. Mean grain size was determined by the intercept method from the SEM micrographs (Topcom Sm-300) where electron dispersive spectroscopy provides information on the compositions of grains and grain boundaries. To perform the electrical measurements, silver contacts were deposited on the sample surfaces. Current–tension measurements were taken using a pulsed high voltage source (Keithley, Model 237). The breakdown electric field (E_b) was obtained at a current density of 1 mA/cm^2. The leakage current density was determined at an electric field equal to 70% of the breakdown field. The nonlinear coefficient (α) was obtained by curve-fitting the log J versus log E plot, using the equation $\log J = \alpha \times \log E + \log K$, i.e. the nonlinear coefficient is the slope of the obtained straight line.

Measurements of real (C') and the imaginary (C'') part of the complex capacitance were performed with a frequency response analyser (HP 4192) using frequencies ranging from 100 Hz up to 1 MHz, with an amplitude voltage of 1 V. A selected varistor sample (as obtained after sintering) was characterized electrically and was afterwards seven times subjected to a thermal treatment in vacuum (0.01 Torr) at 900 °C for 1 h. After each heat treatment, the electrical characterization was repeated. Samples were not taken out of the vacuum before having cooled down to room temperature completely. For comparison, another sample was treated in vacuum at 1100 °C for 3 h.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the CCTO powder calcined at 900 °C for 12 h. Besides the perovskite phase, no secondary phase was observed. Our XRD data confirm the presence of a cubic crystal system [11].

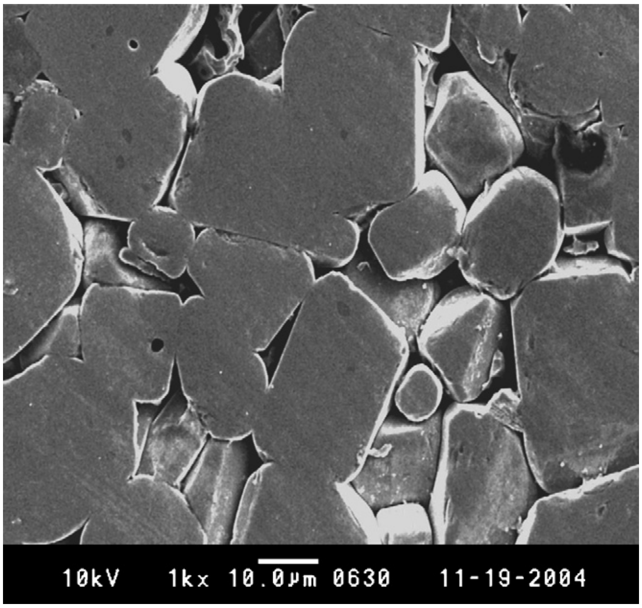

Fig. 2. SEM micrograph for CCTO sample sintered at 1100 °C for 3 h.

In Fig. 2, a typical SEM micrograph from a sintered pellet is given. Mean grain size determined by the intercept method was found as 44 μm. Although no secondary phases were observed in SEM micrographs, electron dispersive spectroscopy revealed that the grain boundaries are CuO enriched relative to the interior of the grains. The densities of sintered samples were obtained by the Archimedes method and are related to the theoretical density of CCTO ($\rho_{\text{theoretical}}$ = 5.07 g/cm^3 [12]). The final densities after sintering were higher than 97%.

It is well-known that oxygen plays a key role in governing metal oxide varistor properties [13–15]. This has been recently again confirmed for strontium titanate varistors by Li et al. [16], the material presents a perovskite structure. They concluded that oxygen chemisorption at the surface of the grain boundaries occurs when a thermal treatment in oxygen

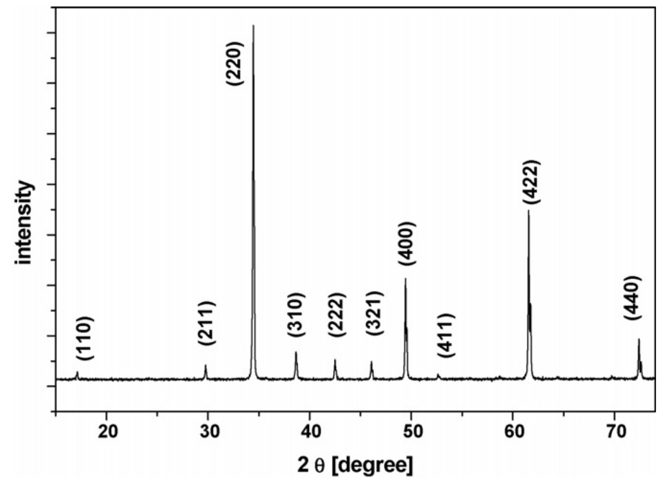

Fig. 1. X-ray diffraction pattern of CCTO powder calcined at 900 °C for 12 h.

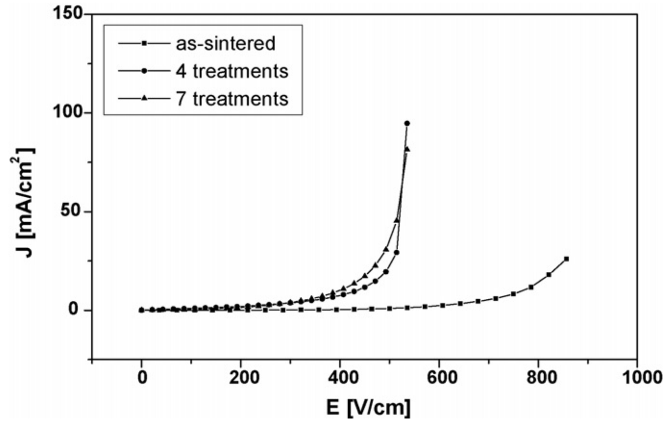

Fig. 3. Current density vs. applied electric field for the varistor sample as-sintered and after four and seven heat treatments in vacuum.

Table 1
Electrical characterization of a selected varistor sample

Number of treatments	Nonlinear coefficient (α)	Breakdown electric field, E_b (V/cm)	Leakage current density (mA/cm^2)
0 (as-sintered)	6.2	535	0.0025
1	2.1	107	0.79
2	1.2	22	0.83
3	1.5	3	0.77
4	1.5	120	0.80
5	3.0	235	0.51
6	2.9	170	0.55
7	3.0	170	0.52

containing atmosphere is performed. This leads to a resistive surface layer, which is the origin of the potential barrier.

When a sintered CCTO varistor ceramic is heat treated in vacuum at 1100 °C for 3 h, which are the same parameters as chosen for sintering, the nonlinear coefficient drops from 6.2 to 3. This can be explained by a removal of chemisorbed oxygen from the grain boundaries as a consequence of the very low oxygen partial pressure during the heat treatment in vacuum. Even treatments for a longer time do not lead to other nonlinear properties. A second heat treatment in air restores the original varistor properties. On the other hand, when reducing the temperature during a vacuum treatment sufficiently, one would expect that the oxygen diffusion along the grain boundaries is more hindered, it takes significantly more time to desorb the oxygen from the grain boundaries. When performing repeated, short heat treatments at such a reduced temperature, a gradual, step-wise degradation of the varistor properties should be observable, i.e. α should gradually tend to reach the constant value 3. It was found experimentally that 900 °C and 1 h are such appropriate parameters.

Fig. 3 shows the current density versus electric field plots obtained for a varistor sample as-sintered, after four and after seven heat treatments in vacuum. A mathematical analysis of the $J \times E$ curves led to somewhat different results, which are summarized in Table 1. The α does not degrade directly from 6.2 to 3, actually during the first three vacuum treatments, the nonlinear coefficient decays much more than expected, the lowest observed value was 1.2. Afterwards, α increases to 3, and final constant values are also reached for the breakdown electric field and the leakage current density. It is interesting to note that the leakage current density is correlated linearly with the nonlinear coefficient. As it can be seen in Fig. 4, high nonlinear coefficients correspond to low leakage currents when operating in the ohmic region, below the breakdown electric field. An ideal varistor possesses an infinitely high α and does not present any leakage current indicating that the barriers at the

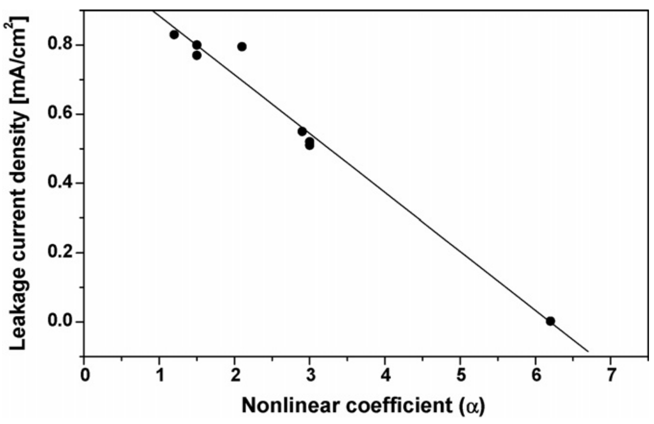

Fig. 4. Linear correlation between the leakage current density and the nonlinear coefficient for a selected varistor sample among the heat treatments in vacuum.

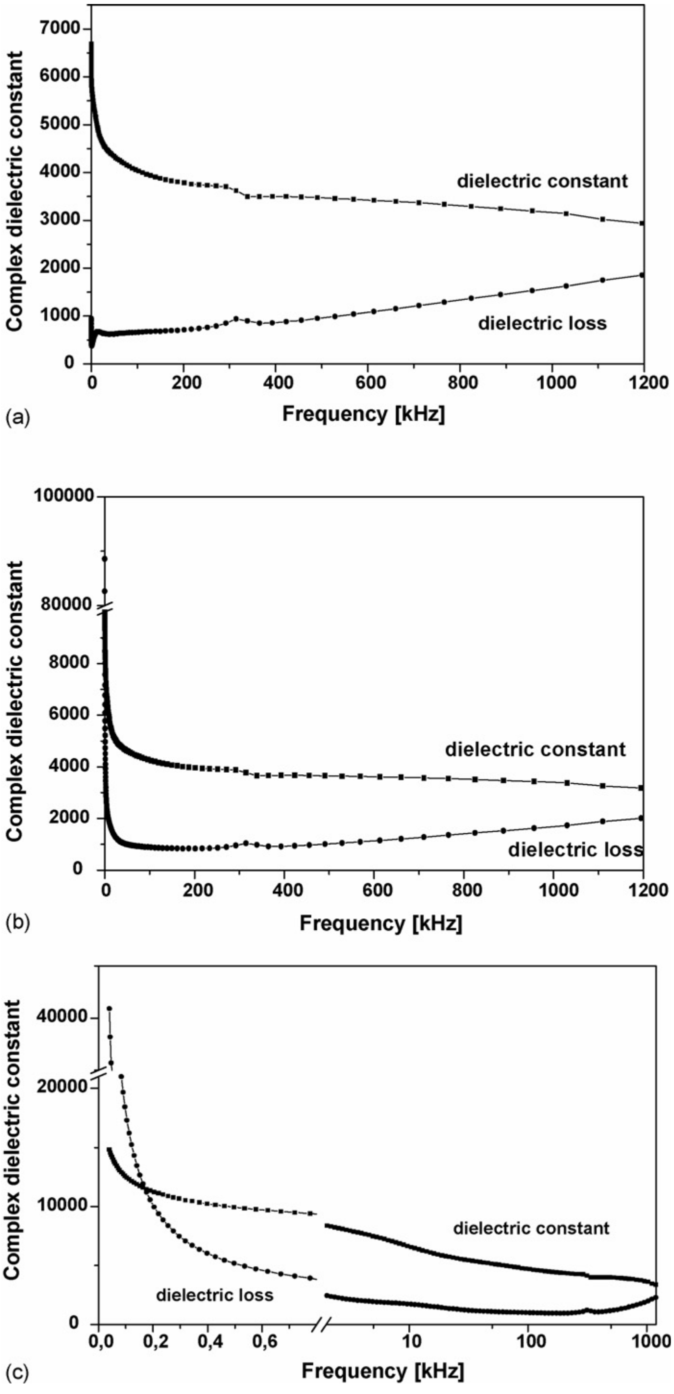

Fig. 5. Complex dielectric constant for a selected varistor sample, characterized: (a) as-sintered; (b) four heat treatments in vacuum; (c) seven heat treatments in vacuum.

grain boundaries are extremely effective. When a varistor presents a pronounced transition range from the ohmic to the nonlinear region, which translates to a high leakage current and a low α, a significant quantity of the grain boundary barriers is not effective. Therefore, the breakdown electric field also decreases with the degradation of α (Table 1) which can be interpreted by a reduced barrier height. One can conclude that there are two processes involved during the heat treatment in vacuum. First, chemisorbed oxygen is removed from the grain boundaries into the vacuum, this process is dominant during the first three treatments. Then, the previously desorbed oxygen is replaced by oxygen coming from the interior of the grains. One has to assume that oxygen vacancies are created and are probably the main lattice defects in that ceramic. However, the newly created grain boundary oxygen cannot be transferred into the vacuum due to charge neutrality restrictions.

Fig. 5 shows the real and imaginary part of the complex dielectric constant for the sample directly after sintering (Fig. 5a) and after the fourth (Fig. 5b) and the seventh heat treatment in vacuum (Fig. 5c). Those data were obtained by impedance spectroscopy. For the relative dielectric constant we obtained values between 4000 and 4700 at 100 kHz. Surprisingly no correlation between the α values and the dielectric constant at a given frequency was found. Considering that commercially available varistors have α values around 50, the nonlinear ohmic properties of our sample are very poor, so that any relationship between α and dielectric constant does not come out clearly. Within the obtained α range, the quantity of charges at the grain boundaries does not vary sufficiently to alter the dielectric constant. As it can be seen from Fig. 5, at very low frequencies the vacuum treated sample shows a dramatically increased dielectric loss and also an apparent higher dielectric constant that both rapidly decay with rising frequency. This effect is attributed to a space charge phenomenon, movable ions exist near the electrode interface. Before the vacuum treatments, silver electrodes were pasted on the polished sample surface, then the sample was annealed at 200 °C for 1 h in ambient atmosphere. These electrodes were not removed when afterwards the heat treatments in vacuum at 900 °C were performed. During these heat treatments, the metal–ceramic interface structure can be changed so that copper atoms from the ceramic enter the silver electrode and vice versa. Such a process creates new crystal defects, space charges and movable ions at the electrode interface, which contribute to the dielectric constant at low frequencies.

Further results could be discovered using the impedance spectroscopy technique at various temperatures. This requires special equipment that allows to store the samples in vacuum during the measurements. In that way, a deep insight in the barrier structure can be obtained. Also experiments using other electrodes should be performed.

4. Conclusions

We have shown by thermal annealing of a CCTO varistor sample in vacuum that at the grain boundaries chemisorbed oxygen plays a key role in governing the nonlinear coefficient. During heat treatments in vacuum at 900 °C, chemisorbed oxygen is removed from the grain boundaries, which can be observed by a degradation of the nonlinear coefficient. When performing further heat treatments, some oxygen from the interior of the grains replaces the previously removed oxygen and α is partially restored. This should lead to more conductive grains due to the remaining oxygen vacancies.

Acknowledgments

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