



Magnetic properties of CCTO doped with GeO₂

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The high dielectric constant presented by CaCu₃Ti₄O₁₂ (CCTO) makes this material promising for industrial applications, in particular for electronic devices. Nevertheless, the preparation method and the doping by oxides has a great influence on the microstructure, and consequently in the dielectric properties. In this work we prepared and studied CCTO doped by germanium oxide, in concentrations up to 10% by weight. X-ray diffraction shows the presence of nanocrystals. The grains and the grain boundaries compositions have been characterized by scanning electron microscopy with energy dispersive X-ray spectrometry mapping. The magnetization measurements show an antiferromagnetic behaviour with a Néel temperature $T_N=25$ K, independent of the GeO₂ doping (up to 6%). Analyses of the high temperature dependence of the magnetic susceptibility show that the increase of the GeO₂ doping decreases the paramagnetic temperature. Dielectric spectroscopy measurements, in the frequency range from 75 kHz to 30 MHz, at room temperature, have been carried out. Cole-Cole model of dielectric relaxation adjusts correctly the data. The results, obtained with the different techniques, indicate that there is the increase of samples grain size up to 6% of germanium oxide, which causes an increase of the real and imaginary parts of complex permittivity.

Keywords: CCTO; Dielectric; Magnetic.

1. INTRODUCTION

CaCu₃Ti₄O₁₂ (CCTO) is a very promising material, because it presents a giant dielectric constant and good stability over a wide temperature range from 100 to 600 K, and frequency up to 1 MHz [1-4]. The potential applications are quite large, particularly in DRAM [5-7] and microwave devices [8], because it reduces the dimensions needed in microelectronic equipment. Nevertheless, it presents a main problem for the technical use in electronic devices due to its large dissipative factor. To explain the dielectric properties of CCTO, it is assumed that insulating surfaces were formed on semi-conducting grains during the sintering process, which are very sensitive to the synthesis parameters. Also, the microstructure and its dielectric properties are strongly dependent on the eventual doping elements and their concentrations [9-12].

Dielectric spectroscopy is a powerful technique to study the structural change of materials. In particular, in this work, we measured the complex permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, and we used it to observe the changes in CCTO, as a function of doping level of GeO₂. The measured quantities, ε' and ε'' , have a direct physical meaning. The real part of the permittivity, ε' , is related to the energy stored and the imaginary part, ε'' , is proportional to the dissipated energy by cycle. So, these quantities have useful information for the electrical and structural characterization of the material.

The magnetic susceptibility (χ) shows an antiferromagnetic behaviour for the undoped CCTO, with a maximum near 25 K (Néel Temperature) [13-16]. At low temperatures, the value of χ for CCTO falls near to 2/3 of its maximum, as expected for a polycrystalline antiferromagnetic material. The antiferromagnetic is due to Cu superexchange interaction through the nonmagnetic Ti⁴⁺ ions. Hence the substitution of the Ti ions by Ge ions should affect the antiferromagnetic interaction between the Cu ions. In this study, the samples' structure has been analysed by XRD and SEM, and correlated with the magnetic properties and the complex permittivity.

2. EXPERIMENTAL

CCTO powder was produced using a solid-state method [1]. Stoichiometric quantities of CaCO₃, TiO₂ and CuO were mixed in a planetary mill during 20 min at 200 rpm. Then, the mixture was calcinated during 12h, at 1050 °C. The obtained ceramic was ball milled, before mixing, with concentrations ranging from 2% up to 10% of GeO₂. The powders were pressed into pellets with 8 mm diameter and thickness about 1 mm and sintered at 1050 °C for 12 h.

X-ray diffraction (XRD) sample patterns were obtained, at room temperature, using a Philips X'Pert system, with K α radiation (Cu α =1.54056 Å) at 40 kV and 50 mA, with a step of 0.02° and a time per step of 3 s. Scanning Electron Microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) mapping was performed in a Hitachi S4100-1 system on the samples, which were covered with a carbon layer of 30 nm before microscopic observation. Using the EDS measurements, it was analysed the chemical elements on the surface and in a few micrometers below it. The magnetic susceptibility was measured from 5 to 300 K in an applied field of 0.5 Tesla, using a vibrating sample magnetometer (VSM) from the Cryogen Free Magnet (Cryogenic) at the University of Aveiro. Complex permittivity measurements were done, at room temperature, over the frequency range from 75 kHz to 30 MHz, on the pellets with opposite sides with silver paint, using a HP 4285A LCR Meter.

3. RESULTS AND DISCUSSION

The presence of CCTO as a single phase for GeO_2 concentration up to 5% is confirmed by XRD analysis, as observed in figure 1. For higher concentrations, the XRD patterns show the presence of secondary phases, identified as CaTiGeO_5 , TiO_2 and CuGeO_3 .

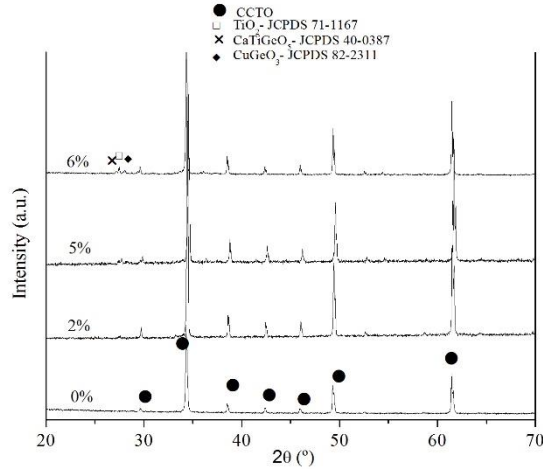


Figure 1 XRD spectrum for the different samples.

The microstructure of the free surfaces of undoped (2a), and 6% (2b) doped samples are shown in figure 2. The morphology of the undoped sample is characterized by loosely linked grains with size ranging from 3 to 6 μm . The surfaces of the samples doped with 5% and 6% are characterized by close packing of the grains with sizes between 10 and 30 μm . The sample doped with 6% has a well-defined grain boundary, rich in Cu and deficient in Ca and Ti, which is confirmed by EDS mapping, as shown in figure 3.

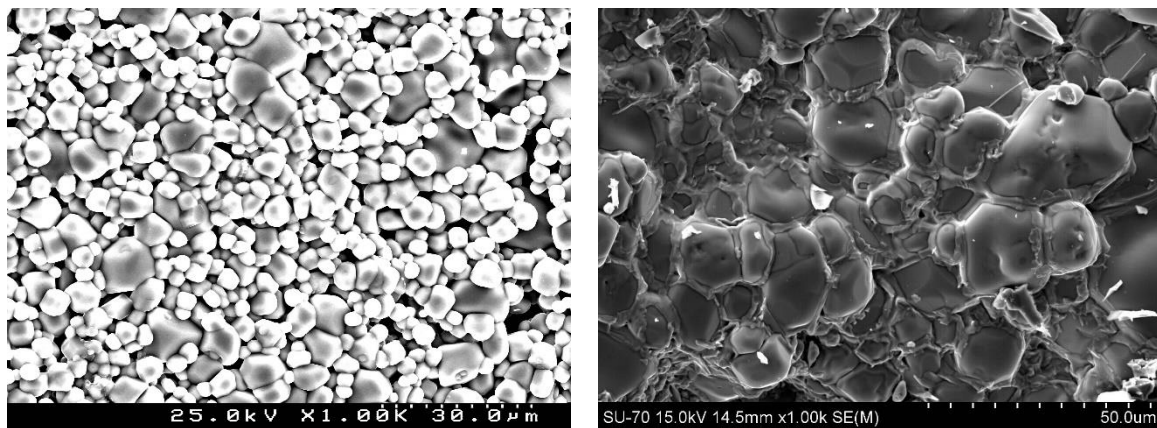


Figure 2 SEM images showing the microstructure of free surfaces of undoped (2a), and 6% (2b) doped samples.

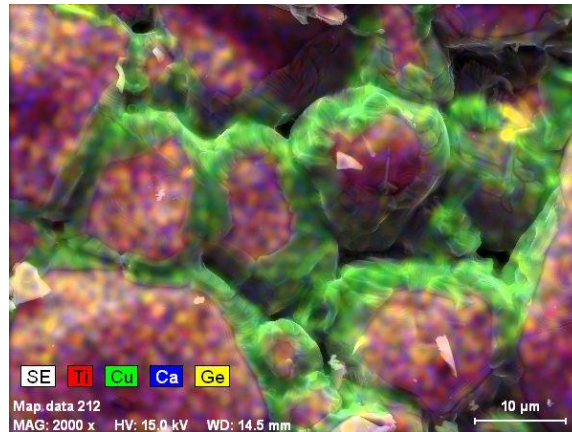


Figure 3 EDS mapping of 6% doped sample.

Figure 4 show the magnetic susceptibility for several samples. The undoped CCTO shows classic antiferromagnetic dependence with the temperature, with a Néel temperature about 25 K, in good agreement with previous works [13-16].

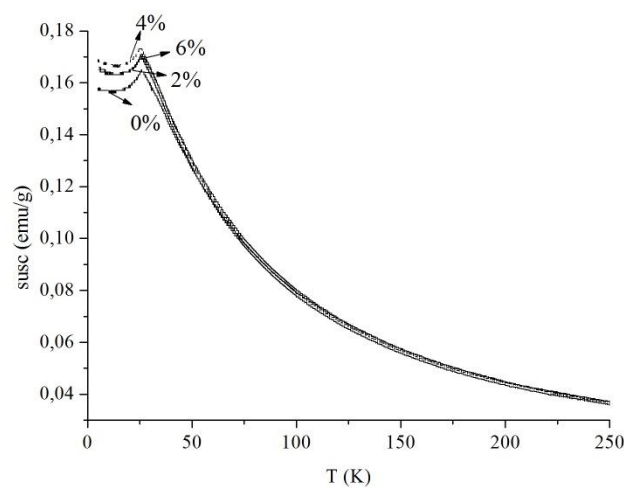


Figure 4 Magnetic susceptibility versus temperature for undoped and samples with 2, 4 and 6 weight % of GeO₂.

This behaviour can be ascribed to the Cu superexchange interaction through the nonmagnetic Ti⁴⁺ ions. The Néel temperature is independent of the GeO₂ concentration for the studied samples (fig. 4), where it is not easy to observe the effect of the GeO₂ in the magnetic structure of the samples. In the inverse of the susceptibility versus temperature (fig. 5), it is observed an increase of the slope with the rise of the germanium concentration.

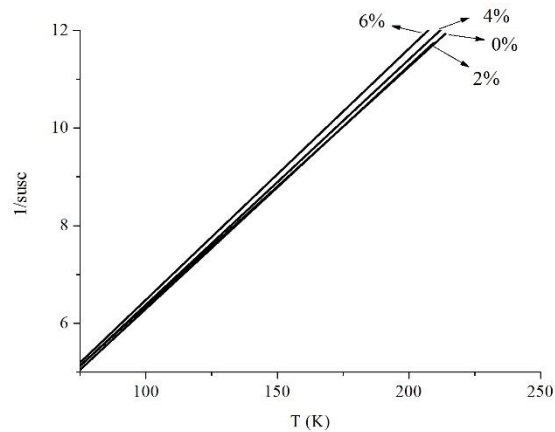


Figure 5 Inverse susceptibility versus temperature of the samples with 2, 4 and 6 weight % of GeO_2 .

The susceptibility data were fitted to a Curie-Weiss equation

$$\chi = \frac{C}{T - \Theta_p} \quad (1)$$

where C is the Curie constant for the Cu ions and Θ_p is the paramagnetic Curie-Weiss temperature. The decrease of the Θ_p values with the growth of the germanium concentration, presented in figure 6, can be ascribed to the diminishing of the antiferromagnetic interaction between the Cu ions, mediated by Ti, due to the substitution of some Ti ions by Ge ions.

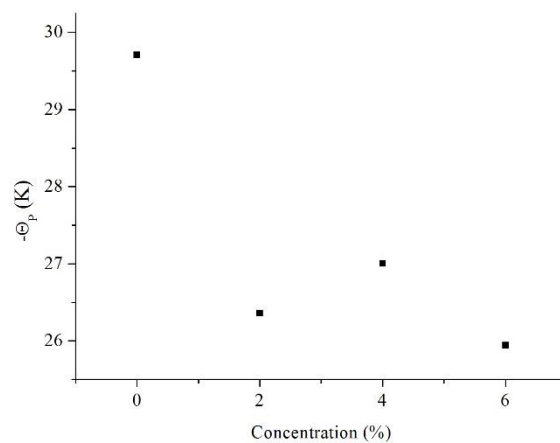


Figure 6 Paramagnetic temperature ($-\Theta_p$) versus GeO_2 concentration.

For the studied compositions it is not observed the ferromagnetic behaviour of the $\text{CaCu}_3\text{Ge}_4\text{O}_{12}$ [16]. In order to analyse the dielectric spectroscopy data, we used the Cole-Cole plot, that is, the graphic of ϵ'' versus ϵ' , as shown in figure 7. A relaxation process is clearly identified, which can be associated to the grain dielectric response [17].

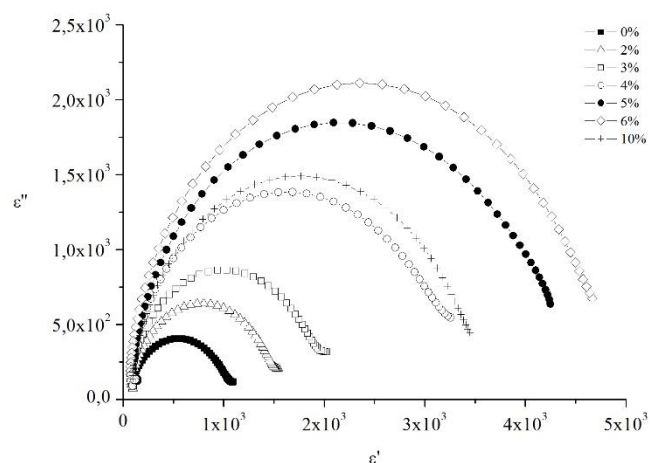


Figure 7 Cole-Cole plot for different concentrations of GeO₂.

The observed arcs are not centred in the ϵ' axis, confirming that a single relaxation time described by the equation of Debye cannot be used to explain this dielectric relaxation. We have analysed the data with the Cole-Cole function [18],

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^{1-\alpha}} \tag{2}$$

In this equation, which is an empirical modification of the Debye equation, ϵ_∞ is the relaxed dielectric constant, $\Delta\epsilon$ the dielectric relaxation strength, τ the relaxation time and α a parameter between 0 and 1 that reflects the dipole interaction. For determining the parameters τ and α , we first calculate the approximate values from the asymptotic part of the data, and then use them as starting values in a non-linear curve fitting algorithm [19]. In figure 8 we present the calculated parameters of the Cole-Cole model of dielectric relaxation, at a constant temperature, for the different germanium oxide concentration [20].

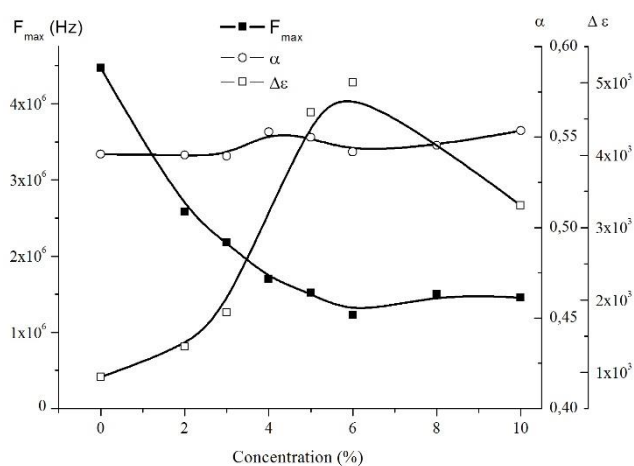


Figure 8 Calculated parameters of the Cole-Cole model of dielectric relaxation, at a constant temperature.

The relaxation frequency, considered as the inverse of relaxation time, decreases till 6%, because the charge carrier's movement becomes frozen with the presence of the extrinsic ion. At this critical concentration, the dielectric strength is maximum, corresponding to the microstructure in which each grain is largely surrounded by exfoliated sheets of Cu-rich phase. Simultaneously, the real and imaginary parts of the complex permittivity reach a maximum at this concentration. The α exponent is not sensible to the doping concentration, but, as is close to 0.5, indicates heterogeneity of the material.

As it was reported before [20], the ϵ' value of polycrystalline CCTO at the high-frequency limit corresponds to the permittivity of the grain volume (ϵ_g), and at the low frequency limit is an apparent value which is given by the following relation:

$$\epsilon_s = \epsilon_{gb} \frac{D}{d} \quad (3)$$

where ϵ_{gb} represents the permittivity of the grain boundary and D and d the thickness of the grain and grain boundary, respectively. We assume, like other authors [16,17], that ϵ_{gb} value is similar to ϵ_g . Assuming that the dimensions of grain boundaries are much smaller than the dimensions of the grains, that is, D/d is very high, we can expect high values for the static dielectric constant of these samples.

4. CONCLUSIONS

Using dielectric spectroscopy measurements and SEM observations we can conclude that the doping of CCTO with germanium oxide at concentration till 6% promotes the increase of samples grain size, which will cause an increase of the real and imaginary parts of complex permittivity. The calculated parameters of the Cole Cole model for dielectric relaxation confirm that behaviour. The presence of the GeO₂ diminishes the superexchange antiferromagnetic interaction between the Cu ions through Ti ions.

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