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Effect of Ca doping on the nonlinear microwave properties of YBCO thin films

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Abstract
We have investigated the microwave properties of a set of four identical $YBa_2Cu_3O_{7-\delta}$ (YBCO) films. One of the films has a 30% Ca-substituted YBCO overlayer, whereas the three others are used as references to highlight the effect of the Ca substitution. The microwave characterization was carried out using the stripline-resonator technique. The R_s of the sample that has a Ca-rich overlayer increased slightly in the linear regime, whereas no significant effect on the nonlinear components and the intermodulation distortion has been observed. We conclude that Ca doping does not significantly improve the nonlinear microwave properties of YBCO films, but the small changes in the linear surface resistance that we observed are discussed in terms of the physics of Ca doping of YBCO.

1. Introduction

High-T_c superconductors (HTSs) and mostly YBCO have been widely studied for their microwave properties that are interesting for devices for wireless applications. The advantage of their low surface resistance is already applied in passive microwave components for cellular base stations. However, a limitation on the incident power these materials can handle still exists. Even at relatively low microwave power a nonlinear behaviour can be responsible for the generation of intermodulation distortion (IMD) in the bandpass of a filter [1]. The origins of the nonlinearities are not yet understood, although making samples with a low linear surface resistance is routine now. Indeed, the linear and nonlinear components of the surface impedance appear to be weakly correlated with each other. Understanding why HTSs become nonlinear is a challenging issue. Its achievement would bring better performance to future devices, a wider range of applications of these devices, and, at the same time, would give information on fundamental aspects concerning the physics of HTSs.

Several techniques are being investigated to improve the power handling capability of the HTSs. Ca substitution has proven to be successful in the case of wires used to carry dc and ac currents [2]. The improvement originates from the diffusion of some Ca atoms in the grain boundaries (GBs) of the HTS films, making them better conductors [3]. The goal of the work reported here is to investigate whether these results can be transferred to the microwave range and nearly single-crystal films. To achieve this objective, Ca-doped YBCO films have been characterized using stripline resonators and the results have been compared with undoped films from the same growth process. The doping is realized by deposition of a $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ surface layer. No significant improvement has been observed in the nonlinear behaviour of Z_s or the IMD, but, surprisingly, the linear R_s shows an increase. Some interpretations are proposed to explain this increase of R_s and the differences between the linear and the nonlinear behaviour.

2. Role of Ca substitution

Conduction in most of the cuprate superconductors and especially YBCO is done by holes that form Cooper pairs or

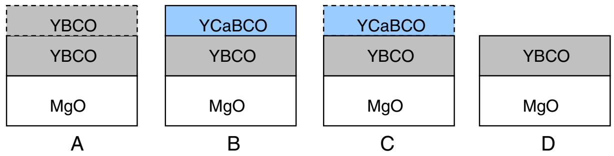

Figure 1. Schematic description of the films under test. The dashed overlayers have been removed by ion-beam etching.

behave as quasiparticles. Increasing the number of carriers is a way to increase the critical current density J_c and thus improve the transport properties of a material. Substitution by selective ions or doping by oxygen has been shown to increase the hole concentration and lead to higher J_c values. Ca as a bivalent atom is particularly interesting as it can be partially substituted for Y [4]. It has been shown that Ca can replace Y up to a limit that is approximately 30% [5]. Replacing Y^{3+} by Ca^{2+} effectively introduces one additional hole per substituted atom. However, this substitution generates oxygen vacancies and disorder that partially compensate the hole generation effect of the Ca. Due to the net overdoping, a homogeneous substitution in the YBCO film decreases the critical temperature T_c.

To prevent such a detrimental effect on T_c, a low level of substitution has to be considered. Annealing under oxygen pressure can also be helpful to compensate the formation of disorder and vacancies. An alternative solution to doping a YBCO film with Ca is to deposit a Ca-substituted YBCO surface layer on top of a YBCO film or create films that comprise alternating YBCO and Ca-substituted YBCO layers [6]. This procedure has been shown to increase substantially the critical current density of polycrystalline films used for dc and ac current transport. In polycrystalline films, the Ca cations have an additional role. They diffuse preferentially along the GBs, increasing their conductivity and the critical current density J_c of the whole film. In addition, this method avoids depression of the T_c that occurs for doping of the YBCO bulk. This method is particularly efficient for films containing high-angle GBs, along which the diffusion of the calcium is easy. For this study, a high level of Ca doping in an overlayer was investigated, to analyse whether it improves the microwave properties.

3. Experiment

3.1. Sample preparation and description

Four 350 nm thick epitaxial YBCO thin films have been grown onto homoepitaxially buffered MgO substrates by electron-beam-assisted thermal coevaporation in atomic oxygen [7]. A post-anneal treatment under a plasma-activated oxygen atmosphere was then applied to each sample to fully oxygenate it. It was confirmed at this stage by dc magnetization that the T_c and J_c values of the four films were very similar ($T_c \sim 89$ K, J_c (77 K) $\sim 3 \times 10^6$ A cm^{-2}). A schematic diagram presented in figure 1 gives the details of the films under test. One of these films (D) was used as a reference for the characterization procedure. On two of these samples (B and C), a 40 nm $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ surface layer was deposited by pulsed laser ablation [2]. This overlayer had a fixed level of Ca substitution of 30%, corresponding to the substitution level of the $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{7-\delta}$ target used in

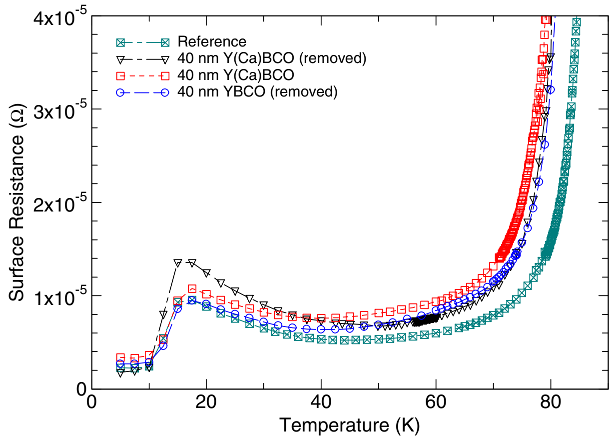

Figure 2. Linear surface resistance as a function of the temperature at 2.3 GHz.

this deposition process. For one of these films (C), the Ca-rich overlayer was removed by ion etching in order to determine whether Ca atoms have diffused in the underlying YBCO film. The last film (A) had an undoped 40 nm YBCO layer deposited on its surface and then removed by ion etching. This procedure investigates the effect of depositing a surface layer by laser ablation (at a higher temperature than the original film growth) and removing it. Each film was subjected to a second annealing in plasma-activated oxygen, as it is essential to ensure a reproducible oxygen content to get systematic results [7], and full oxygenation has proved to improve the microwave properties [8].

The J_c of each film has been measured by dc magnetization as a function of temperature (table 1). The films have then been patterned chemically to form a stripline resonator for microwave characterization at 2.3 GHz [9].

From the variation of the resonant frequency with temperature, a value for the penetration depths λ_0 at 0 K has been extracted as well as the critical temperatures T_c [8], that agree with the T_c from magnetization measurements. The characteristics for each sample are summarized in table 1.

3.2. Surface resistance versus temperature $R_s(T)$

The variation of the effective surface resistance with temperature at low power is presented in figure 2 at 2.3 GHz. The stripline resonator yields an effective surface $R_s = R_s^{\text{film}} + G \tan \delta$. The second term, related to the losses in the dielectric, is usually negligible except for MgO at low T [10]. The local maximum before 20 K is due to MgO. At $T \geqslant 50$ K, the R_s of the YBCO dominates.

The reference sample has the lowest linear R_s. By comparison, the sample that had a YBCO overlayer on its surface that has then been removed exhibits a slightly higher R_s. This could suggest that either the deposition (effectively a high temperature anneal) or the removal of this layer had a damaging effect on the microwave properties of this sample.

The increase in R_s is more pronounced for the two samples that have been doped with Ca. In the case of the sample that still has the Ca-doped layer on its surface, the increase in R_s is the strongest, but it is still significant for the sample that has had this overlayer removed. This suggests that Ca atoms

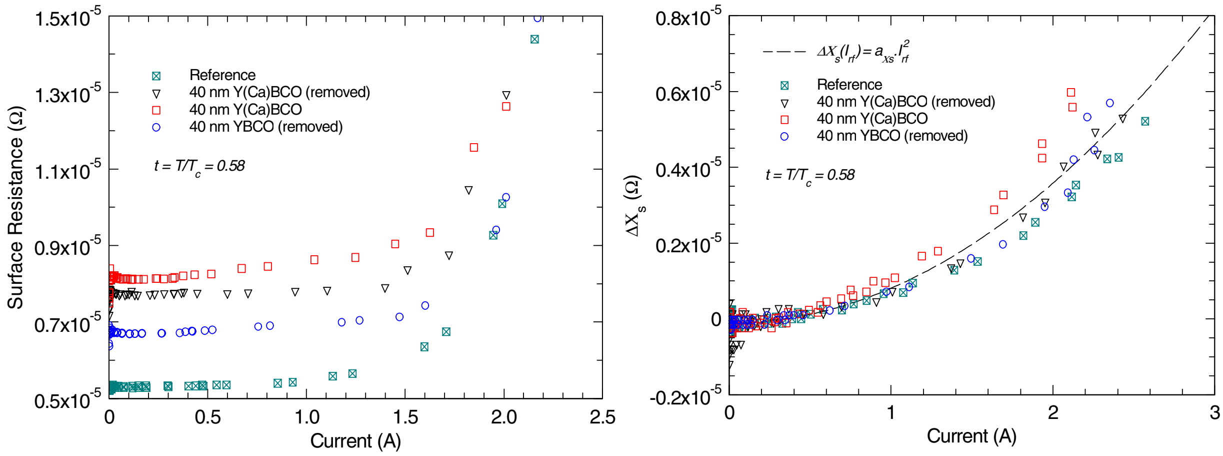

Figure 3. Nonlinear surface resistance $R_s(I_{rf})$ (left) and variation of the nonlinear surface reactance $\Delta X_s(I_{rf})$ as a function of the circulating RF current in the resonator. A fit of $\Delta X_s(I_{rf})$ is given (dashed curve).

Table 1. Characteristics of the four samples under test and R_s at $t = T/T_c = 0.46$.

Sample	t (nm) (YBCO)	t (nm) (overlayer)	O_2 anneal	T_c (K)	J_c (60 K) (A cm^{-2})	J_c (77 K) (A cm^{-2})	λ_0 (nm)	R_s ($\mu\Omega$) $t = 0.46$
A	350	40 (YBCO) (removed)	2	85	1.05×10^7	1.81×10^6	176	6.37
B	350	40 (YCaBCO)	2	83.4	1.28×10^7	1.78×10^6	182	7.60
C	350	40 (YCaBCO) (removed)	2	84.7	1.22×10^7	1.88×10^6	189	7.32
D	350	0	2	89.2	1.46×10^7	3.72×10^6	189	5.68

diffused into the YBCO film or that there is still a thin layer of Ca-substituted YBCO on top of this sample.

3.3. Surface impedance versus RF current

The main objective of this study is to investigate the effect of the Ca substitution on the nonlinear components of $Z_s(T, I_{rf})$. The results of the measurements of the nonlinear surface resistance R_s and the change in the surface reactance ΔX_s are plotted versus the circulating microwave current I_{rf} in the resonator in figure 3. The value of the rf current is calculated from the value of the unloaded quality factor and the insertion loss [11].

No significant change is observed in the behaviour of the nonlinear components of the surface impedance due to the different sample treatments. All samples exhibit the same dependence of R_s on the microwave current, but the curvature of the surface reactance $\Delta X_s(I_{rf})$ for the Ca-doped sample is slightly more pronounced. The Ca-substituted layer leads to slightly larger nonlinearities observable in the surface reactance. For a circulating current of 1 A, ΔX_s has already increased by approximately 7 $\mu\Omega$ more than for the three other samples, which corresponds to an increase of 50% after doping.

Of particular interest is the extension of the linear behaviour of the surface resistance. All samples keep a very linear response versus the microwave current up to approximately $I_{rf} = 1.5$ A. The overdoping with oxygen of these samples and the high epitaxial quality of the YBCO films account for this high power handling. At higher microwave power, the nonlinearity is visible and might be the consequence of flux penetration or a heating effect, which occur for the high value of the RF magnetic field induced by the circulating current [12].

3.4. Intermodulation distortion

Intermodulation distortion measurements have been made [13] in which two closely spaced frequencies f_1 and f_2 inside the -3 dB bandwidth of the resonators are applied. The output powers of the third-order intermodulation products characterized by the frequencies $(2f_1 - f_2)$ and $(2f_2 - f_1)$ are then measured. It has been shown that the IMD power P_{IMD} can be expressed by a power dependence on the input power P_{in}^n, with $2 \leqslant n \leqslant 3$ [14]. This makes the IMD a sensitive probe to the nonlinear properties of a sample, from a very low input power. To correct for different resonator Q and coupling factors and extract the response of the films, some normalizations have been carried out on the measured output power [15, 16]. The results are plotted in figure 4 as a function of the output power of the input frequencies P_{out}, which is proportional to the circulating power. Normalization by Q_0 is given in the left-hand graph of figure 4 and the expected dependence of the quantities shown in the right-hand graph of figure 4 is

$$\frac{P_{IMD}}{r_v(1 - r_v)Q_0} \propto \frac{\Delta X_s}{I_{rf}^2} P_{out}^n \qquad (1)$$

where $\Delta X_s(I_{rf})$ has been plotted in figure 3, r_v is the square root of the insertion loss, and P_{out} is the output power of the input tones.

Figure 4 presents the results of the IMD measurements after scaling by Q and the insertion-loss factor $r_v(1 - r_v)$. For an output power between -40 and -10 dB m, the sample with a Ca-rich overlayer has a 6–10 dB higher IMD signal than the two undoped samples. The sample that has the Ca-rich overlayer removed has an IMD level 4 dB higher than the

Table 2. Conductivity and R_s of the samples and the Ca-doped layer at $t = T/T_c = 0.46$.

	A	B	C	D	Ca doped
σ_1 (S m)	6.82×10^6	7.25×10^6	6.23×10^6	4.98×10^6	1.23×10^7
σ_2 (S m)	1.72×10^9	1.60×10^9	1.48×10^9	1.51×10^9	1.28×10^9
R_s ($\mu\Omega$)	6.37	7.59	7.32	5.68	17.96

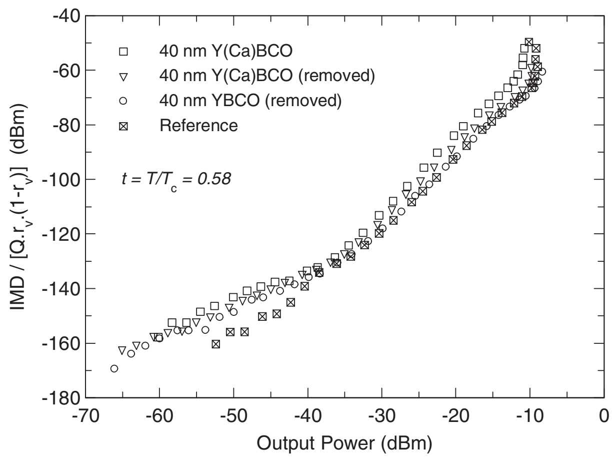

Figure 4. Corrected output power measured at the lower frequency IMD tone as a function of the output power measured at the lower tone.

undoped samples, which might be related to overdoping of the YBCO.

Those results are consistent with the idea that the IMDs depend on the nonlinear contribution of the surface reactance ΔX_s (figure 3), as the Ca-doped sample shows a slightly higher level of intermodulation. The results are also consistent with the previous observation that the different surface treatments have a small effect on the nonlinearities compared to the linear components (figure 3). Besides, the low level of IMDs confirms the good oxygenation of the samples and the careful epitaxial growth.

4. Discussion

Several factors can explain the increase of the linear surface resistance. The high doping level of the Ca-substituted layer, its thickness, and its location play a major role in the microwave response. The quality of the underlying YBCO film is also of particular importance, as it will regulate the diffusion of the Ca atoms. The YBCO layer is considered to be free of high-angle GBs as it has been deposited onto a homoepitaxial buffered MgO substrate. The diffusion of Ca atoms is small, as it mostly occurs due to the presence of GBs [17]. As a consequence, the Ca-rich layer will remain highly doped with a substitution level close to 30%. It has been shown that the superconducting properties get worse with high Ca doping either because of oxygen vacancies, structural disorder, or substitution on the Ba sites [3, 4, 18]. In the microwave range, the linear surface resistance strongly increases as the Ca doping increases, especially in the case of films that are uniformly doped [19, 20]. Indeed, homogeneous Ca substitution only improves the microwave linear R_s for a low level of doping, usually less than 10% [19].

In addition to the high substitution level of the Ca-doped layer, its thickness of 40 nm might also be too large to improve the microwave properties. Obara *et al* [20, 21] have shown recently that the linear microwave properties are improved up to a certain thickness ($\sim$20 nm) but get rapidly worse thereafter even for a lower level of substitution.

From the value of the effective penetration depth and the R_s of the film that has a Ca-doped surface layer and the one that has had a YBCO surface layer removed, the conductivity of the Ca-doped surface layer and its R_s were extracted. The inductance and the resistance per unit length of the doped film can be written as a contribution of the YBCO film and one of the Ca-doped layer [22]. The current distribution J can be considered uniform over the thickness of the film because $\lambda \sim t/2$. Considering also that both samples have the same geometrical inductance, the effective penetration depth of the Ca-doped layer could be extracted by [23]

$$L = \frac{\mu_0}{|I|^2}\left[\int_{t_{\mathrm{YBCO}}}\int_{\mathrm{width}} (\lambda_L^{\mathrm{YBCO}})^2 |J|^2 \,\mathrm{d}S + \int_{t_{\mathrm{Y(Ca)BCO}}}\int_{\mathrm{width}} (\lambda_L^{\mathrm{Y(Ca)BCO}})^2 |J|^2 \,\mathrm{d}S\right] \quad (2)$$

$$R = \frac{1}{|I|^2}\left[\int_{t_{\mathrm{YBCO}}}\int_{\mathrm{width}} \frac{\sigma_1^{\mathrm{YBCO}}}{(\sigma_2^{\mathrm{YBCO}})^2} |J|^2 \,\mathrm{d}S + \int_{t_{\mathrm{Y(Ca)BCO}}}\int_{\mathrm{width}} \frac{\sigma_1^{\mathrm{Y(Ca)BCO}}}{(\sigma_2^{\mathrm{Y(Ca)BCO}})^2} |J|^2 \,\mathrm{d}S\right] \quad (3)$$

where λ is the penetration depth, $\sigma = \sigma_1 + j\sigma_2$ is the conductivity, t_i is the layer thickness, and dS refers to the section of the strip. σ_2 is known from $\lambda_L = (\omega\mu_0\sigma_2)^{-1/2}$. Then, from the resistance per unit length (equation (3)), the quasiparticle conductivity σ_1 is found, which gives an estimate of R_s for the doped layer. The results are summarized in table 2. σ_1 increases with doping and is the highest for the Ca-doped layer, leading to high R_s, whereas the Cooper pair conductivity σ_2 does not seem to change. The use of the effective penetration depth to extract those values may explain the result for σ_2, as it includes some contribution of weak links and other defects, most likely to be present in the case of the doped sample, at the Y(Ca)BCO/YBCO interface. Besides, the doping could increase the density of holes in the Cu–O–Cu chains [24]. Due to its size, the Ca reduces the interlayer coupling strength between CuO_2 planes, resides on the CuO chains and may act on the apical O [25], which could change the distribution of the carriers.

The other important observation of this study is the difference between the linear and the nonlinear behaviour. As observed, the different surface treatments and particularly the presence of the Ca-doped overlayer influenced mostly the R_s in the linear regime, whereas a smaller effect is observed on the nonlinear components of the Z_s or the IMDs. The linear behaviour could result from effects localized at the surface of the sample, whereas a contribution of the whole film is likely to lead to the nonlinear behaviour and the IMDs. This observation supports the hypothesis that the two domains of functioning originate from different contributions. This interpretation is currently being developed [26].

5. Conclusion

Investigations of the effects of doping YBCO films with Ca on their microwave properties have been carried out by using surface layers. The doping did not improve the microwave properties of the sample. This lack of improvement is consistent with the assertion that these high-quality films are free of grain boundaries because that is where Ca doping mainly affects the films. Indeed, as already observed for uniformly doped films, Ca doping rapidly decreases the superconducting and the microwave properties of YBCO. Our surface layer had a high level of substitution close to 30%. No diffusion in the YBCO film was observed because of the high epitaxial quality of this film. Extracting the conductivity and the R_s of the Ca-doped layer, it is shown that at a given reduced temperature the Ca doping seems to increase the quasiparticle conductivity preferentially, leading to a higher value of R_s. This study also allowed us to differentiate between the linear and the nonlinear domain of functioning of the films. The linear regime seems to depend mostly on a surface contribution in opposition to the nonlinear regime that is dependent on the bulk.

Acknowledgments

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References

[1] Oates D E 2001 *Microwave Superconductivity* (*NATO ASI Series*) ed H Weinstock and M Nisenoff (Dordrecht: Kluwer)
[2] Hammerl G *et al* 2001 *IEEE Trans. Appl. Supercond.* **11** 2830–7
[3] Hilgenkamp H *et al* 1999 *Physica* C **326/327** 7–11
[4] Fisher B *et al* 1993 *Phys. Rev.* B **47** 6054–9
[5] Kucera J T and Bravman J C 1995 *Phys. Rev.* B **51** 8582–9
[6] Hammerl G *et al* 2000 *Nature* **407** 162–4
[7] Chew N G *et al* 1995 *IEEE Trans. Appl. Supercond.* **5** 1167
[8] Oates D E *et al* 2003 *IEEE Trans. Appl. Supercond.* **13** 311–4
[9] Revenaz S *et al* 1994 *Phys. Rev.* B **50** 1178–89
[10] Hein M A *et al* 2002 *Appl. Phys. Lett.* **80** 1007–9
[11] Nguyen P P *et al* 1993 *Phys. Rev.* B **48** 6400–12
[12] Gaganidze E *et al* 2003 *J. Appl. Phys.* **93** 4049–54
[13] Oates D E 2003 *EUCAS Conf. (Sorrento, Italy)*
[14] Dahm T and Scalapino D J 1999 *Phys. Rev.* B **60** 13125–30
[15] Vopilkin E A 2000 *Tech. Phys.* **45** 214–20
[16] Dahm T and Scalapino D J 1997 *J. Appl. Phys.* **81** 2002–9
[17] Berenov A *et al* 2002 *Physica* C **372–376** 1059–62
[18] Schlachter S I *et al* 1999 *Physica* C **328** 1–13
[19] Lorenz M, Hochmuth H, Natusch D, Tharigen T, Svetchnikov V L, Zandbergen H W, Schafer C, Kastner G and Hesse D 2000 *Mater. Res. Soc. Symp. Proc.* **603** 163–8
[20] Obara H *et al* 2001 *Appl. Phys. Lett.* **78** 646–8
[21] Obara H *et al* 2002 *Physica* C **378–381** 1419–23
[22] Zhou S-A 1999 *Electrodynamics of Solids and Microwave Superconductivity* (New York: Wiley–Interscience) pp 482–5
[23] Sheen D M *et al* 1991 *IEEE Trans. Appl. Supercond.* **1** 108–15
[24] Bandyopadhyay S K *et al* 1997 *Phys. Lett.* A **226** 237–43
[25] Hsieh C H *et al* 2003 *Physica* C **384** 314–20
[26] Agassi D 2003 unpublished