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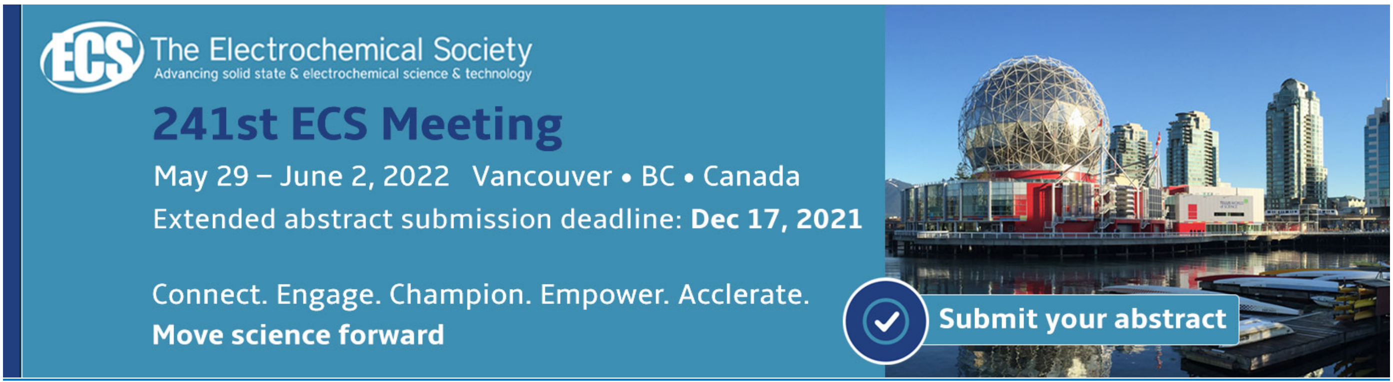

Detection of heterogeneities in single-crystal $CaCu_3Ti_4O_{12}$ using Conductive Atomic Force Microscopy

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Abstract. This paper reports on a conductive atomic force microscopy (C-AFM) investigation to provide local electrical characterization in a single crystal of $CaCu_3Ti_4O_{12}$ (CCTO). The microstructure and dielectric properties were studied and provide evidence for an insulating secondary phase embedded within the semiconducting CCTO matrix. Such insulating electrical heterogeneities cannot be observed with macroscopic measurements such as conventional Impedance Spectroscopy and this study reveals C-AFM to be a powerful tool to assess the electrical homogeneity of semiconducting single crystals such as CCTO.

1. Introduction

The perovskite-related material, $CaCu_3Ti_4O_{12}$ (CCTO), has attracted considerable attention in recent years due to its impressive apparent permittivity value of ~ 10^4-10^5 at 1 MHz, which remains constant in the temperature range ~ 100-600 K.[1,2] The effect has been observed in both single crystals and ceramics. It is now clear that this effect is not an intrinsic property of the material but is related to some form of extrinsic effects, e.g. point and extended defects, contaminants, electrical domain boundaries within grains, grain boundaries, surface layers or non-ohmic electrode contacts. Many of these extrinsic effects have been proposed to lead to the higher than expected permittivity values in

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different oxide-based ceramics, including CCTO.[3] Impedance Spectroscopy (IS) has revealed CCTO ceramics to be electrically heterogeneous and to consist of semiconducting grains and insulating grain boundaries. The giant permittivity effect in CCTO ceramics has been explained using the well-known Internal-Barrier-Layer-Capacitor (IBLC)[4,5] model, however in certain cases a Surface-Barrier-Layer-Capacitor (SBLC) model has been proposed.[6,7] Although the IBLC model works reasonably well for CCTO ceramics, the observation of a giant permittivity effect in CCTO single-crystals[8] remains perplexing as grain boundaries should not be present in single crystals. The origin of the effect in single crystals may therefore be related to some other features not observed in the ceramics, e.g. non-ohmic contacts, modification of crystal surface composition and/or internal boundary layers associated with defects, twins, dislocations, etc.

It is therefore important to study and compare the dielectric properties of CCTO single crystals both with conventional electrical characterisation methods, eg Impedance Spectroscopy, and with high spatial resolution scanning probe methods. However, to date such data have not been produced because of the lack of such characterisation methods. Here we demonstrate the use of a Scanning Probe Microscopy (SPM)-based technique[9,10] to study and compare the electrical and dielectric characteristics of a CCTO single crystal. Useful data can be obtained on application of a bias between the bottom electrode and the conductive AFM tip, which acts, on the sample surface, as a sliding metal contact. This shows conductive-AFM (C-AFM) to be a powerful tool to collect the impedance signal of the nano-device consisting, in our case, of a tip/CCTO/electrode arrangement.[11]

2. Experimental details

Single crystals were prepared, as reported in Ref. **Error! Bookmark not defined.** and 6. After fabrication, the CCTO single crystal slice was polished[12] to eliminate the influence of superficial artefacts in the SPM mapping. Measurements were performed using a back side contact, obtained by silver paint, opposite to the polished surface. Measurements on the nanometre scale were performed by a Digital Instrument D3100 atomic force microscope (AFM) with a Nanoscope V controller operating in air, as illustrated in Figure 1.

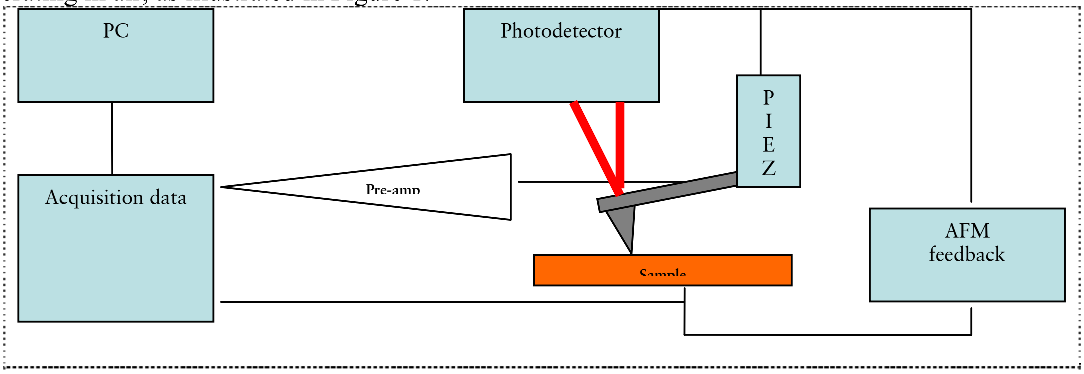

Figure 1. Schematic of the conductive atomic force microscopy module used in this study.

3.Results and Discussion

Laboratory X-ray Diffraction showed the crystal to be single-phase (diffractogram not shown) with all reflections being indexed on the reported space group Im-3. Figures 2 (a) and (b) show the C-AFM morphology and the current map, respectively, of the CCTO single crystal. The morphology image shows the presence of a square-shaped feature within the crystal. The current map shows a dark domain correlated to the morphological feature. This means the feature is on the surface of the sample. Placing the C-AFM tip on the different regions, i.e. on the dark square-faced feature or on the surrounding matrix allowed collection of current versus voltage characteristics for these different regions, as shown in Figure 2c. The current flowing in the dark, square-faced feature was about one order of magnitude lower than that of the surrounding matrix.

The image of this insulating feature in the conductive single crystal reveals electrical heterogeneity within the crystal. In this case, the feature is at the surface of the sample; however, C-AFM also provided evidence of insulating inclusions below the surface of the sample. Figure 3 shows the AFM morphology, Fig. 3 (a), and current image, Fig. 3 (b), where the resistive inclusions are visible only in the current map and not in the morphology image. In this case the insulating inclusion is below the crystal surface.

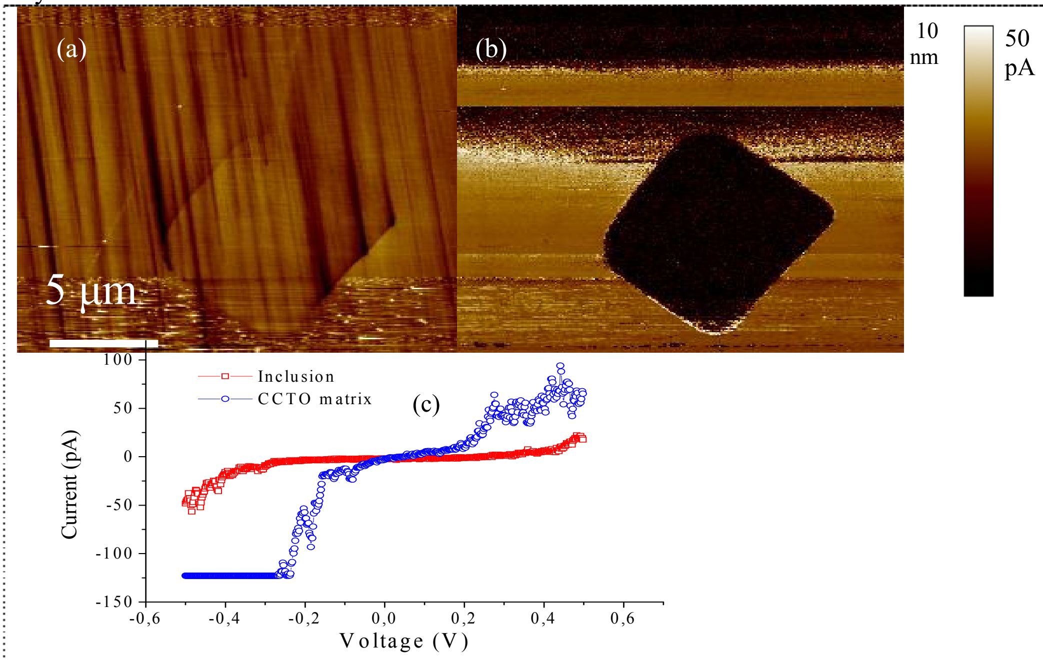

Figure 2. a) AFM morphology where the section of an inclusion is visible, b) current map at 1 V biased where the inclusion appears to be less conducting than CCTO and c) I-V curves acquired on the CCTO single crystal and inside the inclusion. Blue symbols for the CCTO matrix and red symbols for the dark, square-shaped feature. The current flowing in the inclusion is one order of magnitude lower than in the matrix.

These results demonstrate the use of C-AFM to detect the presence of insulating inclusions in a semiconducting matrix such as CCTO. Laboratory XRD failed to detect the presence of any secondary phases, however, based on this study, the volume fraction of the inclusions is small, i.e. < 5 vol% and therefore below the detection limit of laboratory XRD. Further investigations are in progress to identify the composition(s) of these insulating inclusions. This study also shows that C-AFM can be used to detect inclusions both on the surface of the sample and below the sample surface.

Conventional Impedance Spectroscopy cannot identify the presence of such inclusions as the current will prefer to flow through the semiconducting CCTO matrix and therefore detour around the insulating regions. This reveals C-AFM to be a useful complimentary tool to Impedance Spectroscopy when attempting to elucidate the electrical homogeneity and electrical microstructure of complex oxides such as CCTO, especially in cases where isolated resistive inclusions are present in a conducting matrix. It is clear from this study that it is difficult to prepare phase-pure single crystals of CCTO. In the present case, these resistive inclusions cannot be the origin of the giant permittivity effect in CCTO single crystals as they do not form an interconnected network throughout the matrix. However, it is clear that the purity and electrical properties of CCTO single crystals and ceramics are very sensitive to the processing conditions and this may be the reason why some groups have reported a model based on an IBLC model whereas others prefer an SBLC model. Further studies are required to investigate the electrical properties of CCTO single crystals and ceramics as a function of the processing conditions.

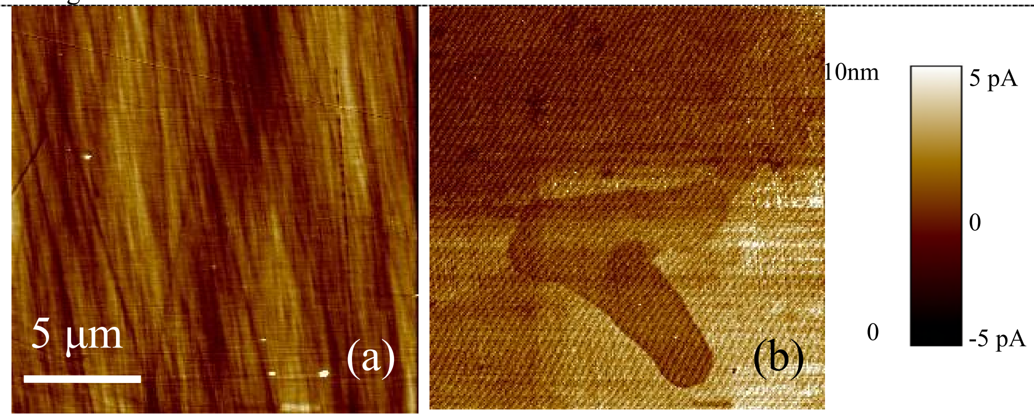

Figure 3. AFM morphology, no features are visible, b) current data map (darker region demonstrates the presence of less conducting part..

4.Conclusion

In conclusion, C-AFM has been demonstrated to image the electrical properties of CCTO single crystal with high lateral resolution. This has allowed electrical characterisation of sub-microstructural features which cannot be obtained from conventional techniques, such as Impedance Spectroscopy. Furthermore, the technique detected insulating features both on the surface of the sample and below the sample surface. This demonstrates that the current spread is sensitive to the electronic structure of the material below the C-AFM tip. Furthermore, this shows that C-AFM is not just a surface technique but is also sensitive to the sample volume cylinder under the tip. The experimental approach presented in this paper could be used to investigate the dielectric properties of a wide class of inhomogeneous materials and will be particularly powerful for detecting insulating regions within a conductive matrix.

5.Acknowledgements.

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