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# Dielectric properties of sol–gel derived $CaCu_3Ti_4O_{12}$ thin films onto $Pt/TiO_2/Si(1\,0\,0)$ substrates

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**Abstract**

The ultrahigh relative dielectric constant ($K'$) values reported for the $CaCu_3Ti_4O_{12}$ bulk ceramics ($10^4$ at RT) joined to their low thermal dependence, no phase transitions are expected between −173 and 330 °C, make this material very promising for capacitor applications and certainly for microelectronics. The interest in the preparation of this material in thin film form is twofold, the understanding of its physical properties and the integration of this high $K'$ oxide with the Si technology. In this work, the preparation of CCTO thin films onto $Pt/TiO_2/SiO_2/Si(1\,0\,0)$ substrates is attempted using sol–gel processing and rapid thermal processing (RTP) at 650 °C. Structural, microstructural and dielectric characterization of the films is performed. The results are commented and discussed on the light of the grain boundary effect on the dielectric constant and the possibility of application of these thin films in microelectronic devices.

*Keywords:* Sol–gel processes; Films; Dielectric properties; Perovskites

## 1. Introduction

Dielectric and magnetic ceramic materials are of increasing interest, as a field of solid-state electronics that continues expanding rapidly. The principal applications for dielectric ceramics are as capacitive elements in electronic circuits and as electrical insulators.[1] High relative dielectric constant ($K'$) ceramics make it possible to noticeably miniaturize passive microwave devices. Their size can typically be reduced in comparing with classical resonators and filters by a factor of $1/\sqrt{K'}$.[2]

The $CaCu_3Ti_4O_{12}$ (CCTO) compound has recently attracted considerable interest in view of its anomalously large dielectric response. It is a cubic perovskite-like phase with space group $Im\overline{3}$. Subramanian and co-workers[3,4] first reported $K'$ values as high as 12,000 of CCTO compound at room temperature. This is possibly related to a Maxwell–Wagner effect due to isolating grain boundaries between semiconducting grains or in the case of single crystals to the blocking of the semiconductivity in dislocations, twins inside the crystal or domain walls.[3,5] Oxides with perovskite structure are well known by their high $K'$ values, which make them appropriate in many technological applications.[6] However, this behavior is generally related to ferroelectric or relaxor phase transitions. However, the reported results for CCTO show that its $K'$ values are high and with small dependence on the temperature.[7,8] Therefore, CCTO based materials are very promising for capacitor applications, microelectronics and microwave devices, where the miniaturization is crucial. Few works have been reported on the preparation of CCTO thin films onto silicon substrates. Most of them are based on physical deposition techniques as pulsed-laser deposition (PLD).[9–11] Scarce works report the use of chemical solution deposition methods (CSD) for the thin film preparation.[12,13]

In this work, we report the CSD preparation of CCTO thin films onto $Pt/TiO_2/SiO_2/Si$ substrates at low temperatures (923 K) using a sol–gel route. The relative dielectric constant ($K'$) and loss ($K''$) were also studied in the range of 100 Hz to 1 MHz as a function of temperature. The results are discussed on the light of the grain boundary effect in the permittivity.

## 2. Experimental methods

A titanium diol-based sol was prepared[14] by refluxing in air and for 1 h titanium di-isopropoxide bis-acetylacetonate $[Ti(OC_3H_7)_2(CH_2COCHCOCH_3)_2]$ and 1,3-propanediol $[HO(CH_2)_3OH]$. Distillation of the 80 vol% of the byproducts of

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reaction was carried out after refluxing. A molar ratio of Ti(IV) to 1,3-propanediol of 1/1 was used. Other two solutions of copper acetate [$Cu(OOCH_3)_2 \cdot xH_2O$] and calcium acetate [$Ca(OOCH_3)_2 \cdot xH_2O$] in 2-ethyl-hexanoic acid [$C_7H_{15}COOH$] were prepared by stirring the acetates in the acid. Molar ratios of any of the acetates to the acid of 1/10 were used. The titanium sol and the copper and acetate solutions were mixed and stirred to obtain a stock solution with a nominal composition of $CaCu_3Ti_4O_{12}$.

Four layers of this solution were successively deposited by spin-coating (2000 rpm/45 s) onto $Pt/TiO_2/SiO_2/(1\,0\,0)Si$ substrates and dried at 350 °C for 60 s. These amorphous films were crystallised by rapid thermal processing (RTP) at 650 °C using cummulative soaking times of 30 + 30 + 60 min.

Grazing incidence X-ray Ddiffraction GIXRD ($\alpha = 2°$) of the prepared films were performed at room temperature using a Siemens D500 diffractometer with Cu anode. The plane view micrographs of the films were obtained by scanning electron microscope (FEG-SEM) using a JSM-6335F NT field emission gun microscope. Thickness of the films was measured from the cross-section SEM micrographs as well as by profilometry in a Talysurf 100 equipment.

Top platinum electrodes with an area of $5 \times 10^{-7}$ m$^2$ were deposited by cold sputtering on the film surfaces using a shadow mask. A LCR-meter HP 4284 A was used to measure dielectric permittivity as a function of temperature (2 °C min$^{-1}$) and at several selected frequencies between 100 Hz and 1 MHz.

## 3. Results and discussion

Fig. 1(a) shows the GIXRD patterns of the crystallized films. In the first 30 min of crystallization at 650 °C, the main peaks of the cubic CCTO phase begins to appear joined to a broad maximum at low $2\theta$ angles due to residual amorphous material. After 60 min of thermal treatment at 650 °C the peaks of the CCTO phase are clearly seen as well as a reduction of the amorphous, but new diffraction peaks at 27.6° and 54.5° $2\theta$ appear, that can be assigned to a $TiO_2$ oxide. A further thermal treatment of 60 min produces an increase in the crystallinity of the CCTO phase.

The plane view SEM image of the CCTO thin film is shown in Fig. 1(b). The film microstructure shows darker regions around small pores. These regions could be the result of diffusion from the $TiO_2$ buffer layer forming the substrate to the surface through the pinholes on the Pt bottom electrode. This would justify the two extra diffraction peaks in the patterns of Fig. 1(a). The inset in Fig. 1(b) shows a surface microstructure area where the grain boundaries have been traced by hand. This microstructure is formed by a mixture of grains with an average grain size of about 150 nm and other smaller grains that some times seems to be included into the large ones, similar to that found out by Fang et al.[15] and related to domains in the case of included small grains. From the cross-section SEM image (not shown) a CCTO layer thickness close to 125 nm can be deduced. This value is in good agreement with the 135 nm thickness obtained from profilometry.

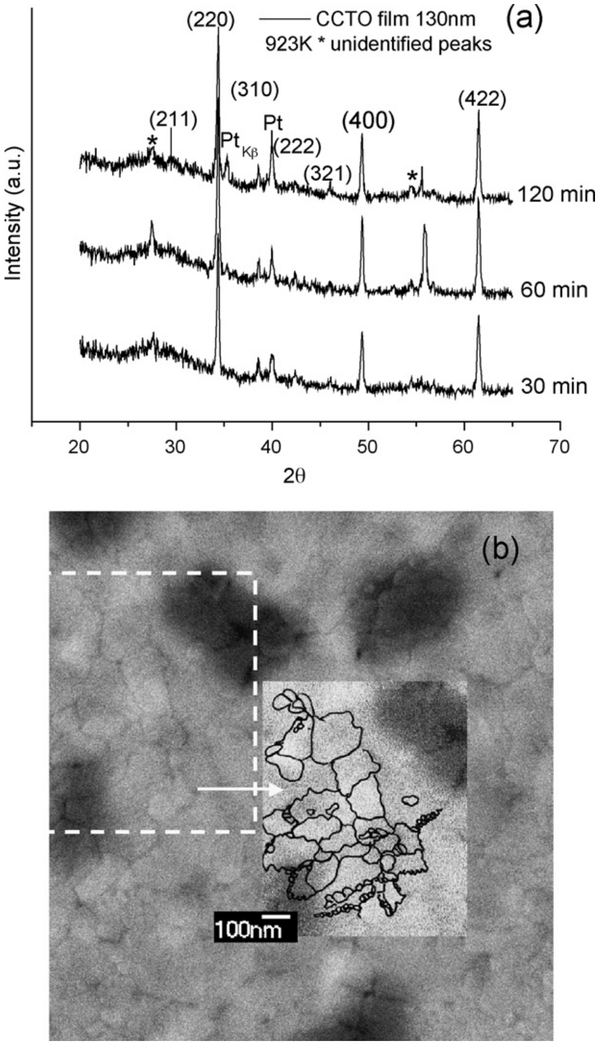

Fig. 1. (a) Grazing incidence X-ray diffraction diagrams of the CCTO films as a function of the crystallization time. The diagrams are displaced in the ordinate values for clarity. The indexing to the ICSD card for the CCTO structure is included. The peaks labeled with (*) are an unidentified phase possibly related to a $TiO_2$ phase. The peaks coming from the substrate are also labeled in the plot. (b) FEGSEM plane view micrograph of the prepared CCTO thin film. The region surrounded by dashed lines is duplicated and the grain-boundaries contour highlighted by hand after eye inspection.

The results of relative permittivity variation with the temperature are included in Fig. 2(a and b). The $K'$ presents three dispersive relaxations (Fig. 2(a)). In the relative dielectric loss ($K''$) Fig. 2(b), three peaks can also be defined. The small one at the highest frequencies and low temperatures corresponds to the relaxation observed at low temperatures in $K'$. Two large peaks appear at the lowest frequencies that at higher frequencies coalescence to produce a single relaxation. In the inset of Fig. 2(b), the loss tangent as a function of temperature at different frequencies is included. The values at maximum are in the range 0.2–0.5 that are lower than those reported for PLD CCTO thin films.[11]

Fig. 3 (open symbols) shows the Arrhenius representation of the frequency of the relative dielectric loss maxima picked from Fig. 2(b). The low temperature relaxation has an activation

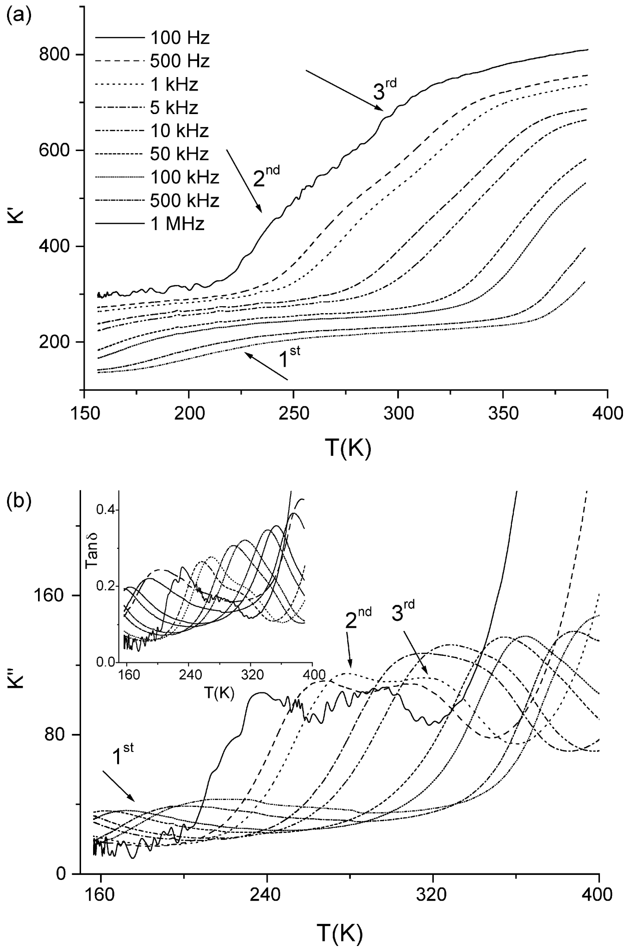

Fig. 2. (a) Relative dielectric constant as a function of temperature at different frequencies from 100 Hz to 1 MHz. The frequency values are depicted in the plot. The arrows signal possible relaxations from 100 Hz to 1 MHz. (b) Relative dielectric loss as a function of temperature at different frequencies. In the inset the loss tangent as a function of temperature at the same frequencies is depicted.

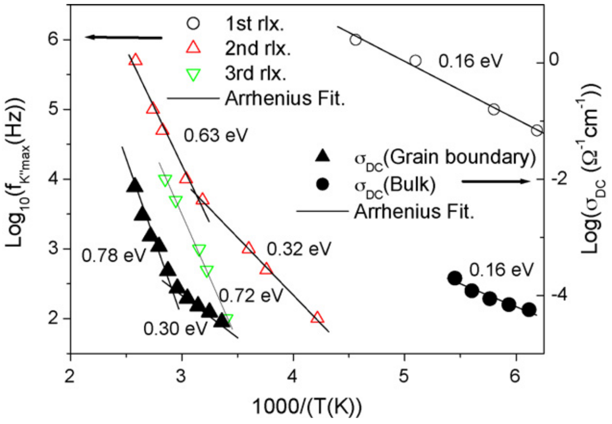

Fig. 3. Arrhenius representation of the relaxation frequency variation as a function of temperature (open symbols) and the D.C. conductivity obtained after applying the Maxwell–Wagner relaxation model (closed symbols). The meaning of the symbols are depicted in the plot as well as the activation energies calculated from the linear fits.

energy of 0.16 eV. The second relaxation presents a change in the activation energy located at 44 °C, giving place to a high temperature activation energy of 0.63 eV and a low temperature activation energy of 0.32 eV. The third relaxation has an activation energy of 0.72 eV. These results indicate that the dielectric response of thin films is dominated by power law in frequency as found by Telesev et al.[16] in epitaxial CCTO thin films.

The equivalent circuit that can explain the observed dielectric relaxations would be formed by three (RC) circuits in series, grain interior, grain boundary and electrode effect. This would gives place two possible relaxations. Following the formalism presented in ref. [16] and considering that the first relaxation is due to the blocking of the grain interior conductivity by the grain boundaries, the relaxation time can be expressed in terms of the equivalent circuit as:

$$\tau = \frac{R_{\mathrm{g}} R_{\mathrm{gb}} (C_{\mathrm{g}} + C_{\mathrm{gb}})}{R_{\mathrm{g}} + R_{\mathrm{gb}}} \tag{1}$$

$R_{\mathrm{g}}$ and $R_{\mathrm{gb}}$, are the resistances of grain and grain boundary, respectively, and $C_{\mathrm{g}}$ and $C_{\mathrm{gb}}$ are the capacitances of the grain and grain boundary, respectively. If it is supposed that $R_{\mathrm{g}} \ll R_{\mathrm{gb}}$ and $C_{\mathrm{g}} \ll C_{\mathrm{gb}}$ Eq. (1) becomes:

$$\tau = R_{\mathrm{g}} C_{\mathrm{gb}} \tag{2}$$

and $C_{\mathrm{gb}} = K'_{\mathrm{S}}\, C_{\mathrm{o}}$ where $K'_{\mathrm{S}}$ is the static relative dielectric constant of the relaxation and $C_{\mathrm{o}}$ is the capacitance of the empty cell. If $C_{\mathrm{gb}}$ is temperature independent $\tau$ should follow the same Arrhenius law as $R_{\mathrm{g}}$. The same simplification can be made for the relaxation between grain boundary and the electrode.

Applying these equations to the relaxations observed in the CCTO films allows to obtain an estimation of the conductivities of grain interior and grain boundary from the values of the static relative dielectric constant and the corresponding relaxation times. To perform the calculations the relaxations observed in the permittivity data as a function of frequency at different temperatures are used. The values of the static relative dielectric constant for the relaxations of the grain interior conductivity and grain boundary conductivity are 265 and 690, respectively. Recently, Shao et al.[17] have studied the microstructure influence on the observed relaxations in CCTO ceramics. They stated that there should be a relaxation due to the domain boundaries that dominates the impedance spectrum at the lowest frequencies. In our thin film, due to the observed bi-modal grain size microstructure and thickness, is possible that the difference between the two low frequency relaxations be small and can be observed in the measuring frequency window. Nevertheless, in thin films the existing asymmetry between the top and bottom electrodes giving place to different Schottky contacts and so different static $K'$ for the relaxation of the grain boundary conductivity can be related to the observation of two low frequency relaxations. For simplicity, in the following discussion just the relaxation with larger peak in Tan $\delta$ (inset in Fig. 2(b)) is taken into account.

In Fig. 3 (solid symbols) the conductivities as a function of the inverse of temperature obtained after applying Eq. (2) are plotted. The grain interior conductivity in the thin film has values much lower than those obtained in bulk ceramics, presenting the same activation energy as the first relaxation time but with a clear departure from linear Arrhenius behavior related to a possible variable-range-hopping type conduction.[18] This conductiviy variation with temperature should be a straight line using $100/T^{1/4}$ abscissa, but in our case this representation slightly improves the linearity. This result can be related to temperature dependence of $C_{\mathrm{gb}}$. The value of activation energy is in good agreement with the results obtained in PLD CCTO thin films by Telesev et al.[16] in the same temperature range.

The results for the grain boundary conductivity showed two regions with different activation energies 0.3 and 0.78 eV for the low temperature and for the high temperature behaviors. The activation energy obtained at the high temperature is in good agreement with the results found out by Chiodelli et al.[19] of 0.76 eV for the grain boundary, but the conductivity values are much higher than those obtained in the later work and than those obtained in ref. [16]. From the results it can be inferred that the difference in conductivity between the grain boundary and grain interior is lower that that obtained in bulk ceramics[5] and PLD thin films.[10,16]

The origin of the increase in homogeneity between the grain interior and the grain boundary must be related to the thin film preparation. The sol–gel technique allows the crystallization of the film in oxygen rich atmospheres and low temperature. The small thickness of the films also enhances the accessibility of the grains to the oxygen producing a decrease in the grain interior conductivity. The easier accessibility to the oxygen and the low crystallization temperature that can prevent the impurity segregation to the grain boundaries, increasing the grain boundary conductivity. At this point, it is interesting to address our attention to the influence of sample thickness onto the derived values of $R_{\mathrm{gb}}$.[20] In the perspective of a back to back double Schottky contact between particles the results of sample thickness influence showed that a reduction of three times in thickness produced a reduction of two orders in magnitude in resistivity with a threshold for sample thickness close to four times the grain size. The low values of $R_{\mathrm{gb}}$ obtained in our thin films can be related the ≈130 nm thickness of our film that is close to once the grain size.

The small thickness of the prepared sol–gel films can be also responsible of the observation in our temperature frequency window of the relaxation at the electrode that is scarcely seen in bulk ceramics and thicker thin films. The low value of $C_{\mathrm{gb}}$ found out here can be related to the effect of the lower conductivity of the grain bulk in the structure of the Schottky contact.

On the other hand, the rather high values obtained for the high frequency relative dielectric constant $(K'_{\infty}) = 130$ in these thin films seems to indicate that the size effects do not have much influence in this property. The equivalent oxide thickness for this sample is 6 nm making this material a promising candidate to be used in high-density DRAM technology.

## 4. Summary

Thin films of 130 nm thickness has been prepared by sol–gel method and RTP at 650 °C. The grain interior conductivity is lower and the grain boundary conductivity larger than the obtained in bulk ceramics or pulsed laser deposition produced thin films. This can be related to the high compositional homogeneity of the films and the low crystallization temperature used. The lower dielectric constant found in comparison with CCTO ceramic can be related to the spreading to the grain interior of the depletion layer in the Schottky contact between grains due to the lower grain interior conductivity. The high value found for the high frequency dielectric constant makes the sol–gel prepared CCTO thin films good candidates for DRAM applications.

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## References

1. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics* (*2nd ed.*). John Wiley & Sons Inc., Massachusetts, 1976, pp. 913–974.
2. Kretly, L. C., Almeida, A. F. L., Fechine, P. B. A., de Oliveira, R. S. and Sombra, A. S. B., Dielectric permittivity and loss of $CaCu_3Ti_4O_{12}$ (CCTO) substrates for microwave devices and antennas. *J. Mater. Sci.-Mater. Electron.*, 2004, **15**, 657–663.
3. Ramirez, A. P., Subramanian, M. A., Gardel, M., Blumberg, G., Li, D., Vogt, T. *et al.*, Giant dielectric constant response in a copper-titanate. *Solid State Commun.*, 2000, **115**, 217–220.
4. Matar, S. F. and Subramanian, M. A., Calculated electronic properties of the mixed perovskite oxides: $CaCu_3T_4O_{12}$ (T = Ti, Cr, Mn, Ru) within the DFT. *Mater. Lett.*, 2004, **58**, 746–751.
5. Sinclair, D. C., Adams, T. B., Morrison, F. D. and West, A. R., $CaCu_3Ti_4O_{12}$: one-step internal barrier layer capacitor. *Appl. Phys. Lett.*, 2002, **80**, 2153.
6. Subramanian, M. A., Li, D., Duan, N., Reisner, B. A. and Sleight, A. W., High dielectric constant in $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ Phases. *J. Solid State Chem.*, 2000, **151**, 323–325.
7. He, L., Neaton, J. B., Vanderbilt, D. and Cohen, M. H., Lattice dielectric response of $CdCu_3Ti_4O_{12}$ and $CaCu_3Ti_4O_{12}$ from principles. *Phys. Rev. B*, 2003, **67**, 012103-1–012103-4.
8. Kolev, N., Bontchev, R. P., Jacobson, A. J., Popov, V. N., Hadjiev, V. G., Litvinchuk, A. P. *et al.*, Raman spectrocopy of $CaCu_3Ti_4O_{12}$. *Phys. Rev. B*, 2002, **66**, 132102.
9. Fang, L. and Shen, M., Effects of postanneal conditions on the dielectric properties of $CaCu_3Ti_4O_{12}$ thin films prepared on Pt/Ti/$SiO_2$/Si substrates. *J. Appl. Phys*, 2004, **95**(11), 6483.
10. Fang, L., Shen, M. and Yao, D., Microstructure and dielectric properties of pulsed-laser-deposited CaCu3Ti$_4$O$_{12}$ thin films on LaNiO3 buffered Pt/Ti/SiO2/Si substrates. *Appl. Phys. A*, 2005, **80**, 1763.
11. Fang, L. and Shen, M., Deposition and dielectric properties of $CaCu_3Ti_4O_{12}$ thin films on Pt/Ti/$SiO_2$/Si substrates using pulsed-laser deposition. *Thin Solid Films*, 2003, **440**, 60.
12. Bermúdez, J. A., *Síntesis y caracterización de materiales en el sistema* $Ca_{1-x}R_xCu_3Ti_4O_{12}$ (*R = Mg, Sr,Zn*). M.Sc. thesis. Universidad de Puerto Rico, 2004.
13. Lu, W., Feng, L., Cao, G. and Jiao, Z., Preparation of $CaCu_3Ti_4O_{12}$ thin films by chemical solution deposition. *J. Mater. Sci.*, 2004, **39**, 3523.
14. Calzada, M. L., Sirera, R., Carmona, F. and Jiménez, B., Investigations of a sol–gel process for the prepration of lead titanate materials. *J. Am. Ceram. Soc.*, 1995, **78**(7), 1802.
15. Fang, T. T. and Liu, C. P., Evidence of internal domains for inducing the anomalously high dielectric constant of $CaCu_3Ti_4O_{12}$. *Chem. Mater.*, 2005, **17**, 5167.
16. Telesev, A., Brooks, C. M., Anlage, S., Zheng, H., Salamanca-Riba, L., Ramesh, R. *et al.*, Evidence of power-law frequency dependence of intrinsic dielectric response in the $CaCu_3Ti_4O_{12}$. *Phys. Rev. B*, 2004, **70**, 144101.

17. Shao, S. F., Zhang, J. L., Zheng, P., Zhong, W. L. and Wang, L., Microstructure and electrical properties of $CaCu_3Ti_4O_{12}$ ceramics. *J. Appl. Phys.*, 2006, **99**, 084106.
18. Zhang, L. and Tang, Z. J., Polaron relaxation and variable-range-hopping conductivity in the giant-dielectric-constant material $CaCu_3Ti_4O_{12}$. *Phys. Rev. B.*, 2004, **70**, 174306.
19. Chiodelli, G., Massarotti, V., Capsoni, D., Bini, M., Azzoni, C. B., Mozzati, M. C. *et al.*, Electric and dielectric properties of pure and doped $CaCu_3Ti_4O_{12}$ perovskite materials. *Solid State Commun.*, 2004, **132**, 241.
20. Adams, T. B., Sinclair, D. C. and West, A. R., Characterization of grain boundary impedances in fine- and coarse-grained $CaCu_3Ti_4O_{12}$ ceramics. *Phys. Rev. B*, 2006, **73**(9), 094124.