I. Introduction

The ternary oxide compound CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is a 1 : 3 A-site ordered perovskite (A$'$$'$A$''$$''$B) where the oxygen octahedra are strongly tilted and the A$'$ site Cu cations adapt a fourfold square-planar coordination. The CCTO unit cell is a doubled simple perovskite cell and is commonly indexed as cubic Im$ar{3}$. The octahedral tilting can be described as $a'$ $a'$ $a'$ in the Glazer notation.\(^3^\)\(^-^\)\(^5^\)

CCTO has attracted considerable interest due to its giant dielectric permittivity values\(^6^\)-\(^1^\)\(^1^\) in polycrystalline ceramics the highest values reported are $\approx$ 300 000.\(^1^\)\(^2^\) It is now well established that such high permittivity values have an extrinsic origin.\(^1^\(^3^\)-\(^1^\(^4^\) In ceramics, an internal barrier layer capacitor (IBLC) structure has been proposed that is made up of semiconducting grains and insulating grain boundaries (GBs), where the extrinsic giant permittivity $\varepsilon_{GB}$ would be called a GB effect.\(^1^\(^5^\) In single crystals and epitaxial thin films, giant permittivity can be associated with an extrinsic electrode-sample interface effect,\(^1^\(^6^\)-\(^1^\(^7^\) which can also contribute to the giant permittivity in ceramics.\(^1^\(^8^\) The intrinsic relative dielectric permittivity, $\varepsilon_{ib}$ of bulk CCTO was reported to be around 100.\(^1^\(^4^\) While this is considerably lower than the giant extrinsic values, it is still higher than would be expected in a non-ferroelectric material based on the polarizabilities of the constituent atoms\(^1^\(^9^\) as predicted by the Clausius–Mossotti equation (i.e., $\varepsilon_{ib}$ in CCTO is expected to be $\approx$ 48). The difference in electrical conductivity between the GB and bulk areas in CCTO is large: the GB charge transport activation energy $E_A$ is about 0.5–0.8 eV, while the bulk $E_A$ is about 10–100 meV.\(^1^\(^5^\)-\(^2^\)\(^0^\) Additionally, the nominal resistance of the GB and bulk areas vary by a factor of up to $\approx$ 10\(^5^\). Considering that the GB areas are expected to be thin layers the actual difference in resistivity may be even more dramatic. It was shown previously that this distinct ceramic IBLC structure becomes more pronounced during the ceramic sintering process and is associated with segregation of Cu towards the GB areas.\(^2^\(^1^\) More recently it was shown that the interior conducting grain phase of CCTO in fact grows out of an insulating matrix during sintering, most likely by segregation of Cu out of the conducting areas.\(^2^\(^2^\) Here, in this work, such Cu segregation is explicitly associated with a defect mechanism, which offers a plausible explanation for the large differences in conductivity between the bulk and GB regions. A second defect mechanism is associated with the Ca–Cu anti-site defects and the increased $\varepsilon_{ib}$ bulk permittivity.

In the literature the CCTO bulk semiconductivity has been associated with quite different and often contradictory defect mechanisms for this nominally insulating compound. It is generally agreed that deviations from the nominal CaCu$_3$Ti$_4$O$_{12}$ stoichiometry must exist in bulk areas to explain their semiconductivity, and that the insulating GBs would exhibit smaller or no deviations.\(^2^\(^3^\)-\(^2^\(^5^\) Several defect mechanisms suggested in the literature are contradictions because they imply that different types of bulk semiconductivity are occurring, i.e. n-type electron or p-type hole conduction. Semiconductivity in bulk CCTO could potentially rely on mixed valence Ti$^{3+}$/Ti$^{4+}$ or Cu$^{1+}$/Cu$^{2+}$ (n-type), or Cu$^{2+}$/Cu$^{3+}$ (p-type) conduction. All defect mechanisms, solid solutions and possible compensation mechanisms reported in the literature\(^2^\(^1^\)-\(^2^\(^5^\) are summarised below in eqn (A–D). A further
are more similar
is supported by findings of (i) Cu loss;\textsuperscript{25,31} (ii) the presence of
and 30), respectively, both from XPS studies, whereas model (D)
are consistent with the detection of Cu\textsuperscript{+} (ref. 29) and Ti\textsuperscript{3+} (ref. 29
vacancies, which is a common phenomenon in perovskite and
been mentioned in the literature, but may be applicable in Cu-
Cu\textsuperscript{2+} to Cu\textsuperscript{3+}. Eqn (E) corresponds to excess Cu and compensa-
tion occurs by Cu\textsuperscript{2+} occupying Ti sites and the formation of
reoxidation,
\[42x296]i.e., an internal redox process takes place. Only the redox
process is displayed in eqn (C) as the high temperature Cu
reduction is identical to eqn (B). Eqn (D) represents the loss of
Cu due to Cu segregation or volatilisation and the formation of
Cu vacancies. Compensation occurs \textit{via} the partial oxidation of
Cu\textsuperscript{2+} to Cu\textsuperscript{3+}. Eqn (E) corresponds to excess Cu and compensa-
tion occurs by Cu\textsuperscript{2+} occupying Ti sites and the formation of
oxygen vacancies. Alternatively, compensation in eqn (E) could
also occur \textit{via} oxidation of Cu\textsuperscript{2+} to Cu\textsuperscript{3+} and fewer oxygen
vacancies would form. Models (A), (B) and (C) are supported by the
propositions of n-type conduction.\textsuperscript{24,28} Processes (B) and (C)
are consistent with the detection of Cu\textsuperscript{+} (ref. 29) and Ti\textsuperscript{3+} (ref. 29
and 30), respectively, both from XPS studies, whereas model (D)
is supported by findings of (i) Cu loss;\textsuperscript{25,31} (ii) the presence of
Cu\textsuperscript{3+} seen in XPS studies,\textsuperscript{25} and (iii) p-type bulk semiconductivity
determined from Hall effect measurements.\textsuperscript{17} Eqn (E) has not
been mentioned in the literature, but may be applicable in Cu-
rich GB areas. Furthermore, Ca\textsuperscript{2+} and Cu\textsuperscript{2+} anti-site defects have
been proposed to be the origin of the high dielectric permittivity
in CCTO,\textsuperscript{32} despite the considerable mismatch between the
ionic radius of Ca\textsuperscript{2+} (XII coordination: 1.35 Å) and Cu\textsuperscript{2+} (IV
square planar coordination: 0.62 Å). Another possible anti-site
defect mechanism may be Cu–Ti disorder, where the ionic radii
are more similar \textit{i.e., Cu\textsuperscript{2+} (VI: 0.73 Å)\textsuperscript{33} and Ti\textsuperscript{4+} (VI: 0.605 Å), and
both cations are known to exist in a IV square–planar
coordinated. For the unusual square planar IV coordination of
Ti\textsuperscript{4+} in CCTO\textsuperscript{34} the ionic radius may be assumed to be similar
to that for the Ti\textsuperscript{4+} tetrahedral IV coordination (0.42 Å),\textsuperscript{35}
because two such ionic radii are reported the same for IV Cu\textsuperscript{2+} as
well.\textsuperscript{35}

It is clear that the issue of non-stoichiometry in bulk CCTO is
not resolved yet and clear experimental evidence for any of the
above mentioned defect mechanisms [eqn (A–E)] is missing
despite considerable research efforts in recent years. The work
presented here is therefore intended to shed light on the defect
chemistry and non-stoichiometry of CCTO by conducting a
phase diagram study. Evidence is presented for two different
defect mechanisms, and their corresponding solid solutions,
which cause non-stoichiometry in CCTO. Powder and ceramic
samples of different composition within the ternary CaO–CuO–
TiO\textsubscript{2} phase diagram are analysed, where the CCTO lattice
parameter \(a\) and dielectric properties, such as intrinsic bulk
resistivity (\(\rho\infty\)) and permittivity (\(\varepsilon_\infty\)), of the ceramics were
determined using X-ray diffraction (XRD) and impedance
spectroscopy (IS), respectively. It is demonstrated herein,
that only by relating such lattice and intrinsic dielectric parameters
to each other can exceptionally small levels of CCTO non-
stoichiometry be revealed. Data from the individual phase
diagram study, lattice parameter determination from XRD and
IS experiments alone show no or only inconclusive trends, and a
combined study relating the results of all three techniques
to each other is required to understand the defect mechanisms,
non-stoichiometry and electrical properties of CCTO ceramics.
Although evidence for small scale non-stoichiometry in CCTO
is presented, the stoichiometric nomenclature of CaCu\textsubscript{3}Ti\textsubscript{4}O\textsubscript{12}
(CCTO) will be used throughout this work.

II. Experimental

Powder of various compositions within the ternary CaO–CuO–
TiO\textsubscript{2} phase diagram were synthesised from different amounts
of dried high purity reagents of CaCO\textsubscript{3} (Aldrich, 99.995%
purity), CuO (Aldrich, 99.99%) and TiO\textsubscript{2} (Sigma-Aldrich,
99.99%). Starting reagents of lower purity were found to be
inappropriate for revealing the small intrinsic defect mechan-
isms in CCTO. Mixing and grinding of the precursor oxides
was performed using an agate pestle and mortar. At least 3
successive mixing/grinding and heat treatment cycles were
required to fully react and homogenise each composition. The
powder reaction was achieved at 1000 °C in a Lenton muffle
furnace on Pt foil in successive cycles of 12 and 8 h, until
the phase compositions observed by XRD did not change any
further. All powders were synthesised simultaneously to
exclude differences in the processing conditions. A small
portion of each powder was heated again at 1100 °C for 12 h to
enable investigation of the phase diagram for both 1100 and
1000 °C fired materials. The former is the most frequently
used densification–sintering temperature for CCTO ceramics,
whereas CCTO synthesis is most commonly achieved at \(\approx\)
1000 °C. Rapid cooling was performed for all powders by
swiftly removing the Pt foils, on which the powders were
placed, from the furnace and exposing them to ambient

\[
\text{O}_2^- + 2\text{Ti}^{4+} \rightarrow \text{V}^0_\text{Ti} + 2\text{Ti}^{3+} + 1/2\text{O}_2 \uparrow : \\
\text{Ca(Cu}_3\text{)Ti}_4 \rightarrow \text{u} + \text{Ti}_4 \rightarrow \text{O}_12 - w/2 \quad (A)
\]

\[
3\text{Cu}^{2+} \rightarrow \text{Cu}^{+} + \text{Cu}^{2+} + \text{Cu} + \uparrow : \\
\text{Ca(Cu}_2\text{)Ti}_3 \rightarrow \text{u} + \text{Cu}_2 \rightarrow \text{Ti}_4 \rightarrow \text{O}_12 \quad (B)
\]

\[
\text{Cu}^+ + \text{Ti}^{4+} \rightarrow \text{Cu}^{2+} + \text{Ti}^{3+} : \\
\text{Ca(Cu}_2\text{)Ti}_4 \rightarrow \text{u} + \text{Ti}_4 \rightarrow \text{O}_12 \quad (C)
\]

\[
3\text{Cu}^{2+} \rightarrow \text{V}^0_\text{Cu} + \text{Cu}^{3+} + \uparrow : \\
\text{Ca(Cu}_3\text{)Ti}_3 \rightarrow \text{u} + \text{Cu} \rightarrow \text{O}_12 \quad (D)
\]

\[
\text{O}_2^- + 2\text{Ti}^{4+} \rightarrow \text{V}^0_\text{Ti} + 2\text{Ti}^{3+} + 1/2\text{O}_2 \uparrow : \\
\text{Ca(Cu}_3\text{)Ti}_4 \rightarrow \text{u} + \text{Cu}_2 \rightarrow \text{O}_12 - w \quad (E)
\]
conditions on a brass block. Phase analysis of each composition was performed by XRD using a high-resolution STOE STADI-P diffractometer (STOE & Cie GmbH, Darmstadt) with an image plate detector and Cu-Kα1 radiation in transmission mode, operated at 40 kV and 40 mA. Data were collected using WinXPow software. Small amounts from all of the 1000 and 1100 °C fired powders were mixed with an internal Si standard, and high angle XRD patterns were collected using the STOE STADI-P diffractometer with a position sensitive detector (PSD). The CCTO lattice parameters were refined from three or more high angle CCTO reflections using a linear least squares fitting routine provided within the WinXPow software package. For each composition, pellets were pressed from freshly crushed and ground powders using a uni-axial hydraulic press (1 ton) and all were simultaneously sintered at 1100 °C on Pt foil for 12 h. This is the same holding time used for the 1100 °C phase diagram and the lattice parameter study on the powders. This renders comparable the CCTO 1100 °C powder lattice parameter \(a\) and the ceramic dielectric parameters such as intrinsic bulk resistivity \(\rho_b\) and permittivity \(\epsilon_b\). As shown below, this is a viable approach to reveal the clear dependencies between \(a-\rho_b\) and \(a-\epsilon_b\).

For dielectric characterisation, pellets were covered on both sides with Au electrodes using a dc sputtering technique. Alternating current IS was carried out at 10–500 K between 1 Hz–2 MHz using an Agilent E4980A LCR meter, a Solartron 1296/1255 impedance analyzer, both with 100 mV amplitude ac voltage signal, an Oxford Instruments closed-cycle He refrigerator and a custom built tube furnace equipped with a Eurotherm 2216 temperature controller. The real and imaginary parts of the complex impedance \((Z^*)\) were measured and converted into the complex capacitance \((C^*)\) and electric modulus \((M^*)\) formats using the standard conversion. Scanning electron microscopy (SEM) images were collected with a JEOL JSM 6400 microscope, which was equipped with a facility for quantitative energy dispersive analysis of X-rays (EDAX). Scanning tunnelling microscopy (STM) micrographs of the ceramic surfaces were collected using a Digital Instrument D3100 atomic force microscopy (AFM) with a Conductive Atomic Force Microscopy (C-AFM) module.

### III. Results

#### A. Phase analysis in the CaO–CuO–TiO₂ ternary phase diagram

The CaO–CuO–TiO₂ ternary phase diagram for the heat treated powders at 1100 °C is presented in Fig. 1, where the filled black symbols represent all of the compositions investigated. Numbered symbols represent the compositions analyzed by the determination of their lattice parameter and IS. On the full red lines two phases are present. Dashed blue lines represent CCTO compositions with potential Ca, Cu or Ti loss: \(\text{Ca}_1\text{..}_x\text{Cu}_y\text{Ti}_4\text{O}_{12}\), \(\text{CaCu}_3\text{..}_y\text{Ti}_4\text{O}_{12}\) and \(\text{CaCu}_3\text{..}_z\text{Ti}_4\text{O}_{12}\). Green arrows indicate the direction of the potential solid solutions, see eqn (B–E). Such arrows are much larger than any of the expected small solid solutions and may be regarded as a guide to the eye.

![Fig. 1 Ternary CaO–CuO–TiO2 phase diagram. Filled black symbols represent all of the compositions investigated. Numbered symbols represent the compositions analyzed by the determination of their lattice parameter and IS. On the full red lines two phases are present. Dashed blue lines represent CCTO compositions with potential Ca, Cu or Ti loss: Ca₁₋ₓCuₓTi₄O₁₂, CaCu₃₋₁ₓTi₄O₁₂ and CaCu₃Ti₄₋₂ₓO₁₂. Green arrows indicate the direction of the potential solid solutions, see eqn (B–E). Such arrows are much larger than any of the expected small solid solutions and may be regarded as a guide to the eye.](image-url)
black symbols within the main triangle represent the specific Ca–Cu–Ti cation ratios (at%) of all of the samples investigated. All numbered compositions (1–8) were investigated in more detail by determination of the lattice parameter using XRD and by IS on pellets sintered at 1100 °C.

The only single phase composition detected by XRD phase analysis within the main triangle was the CCTO phase, marked as composition 1. CaTiO$_3$ (CTO) was the only significant single phase on the CaO–TiO$_2$ binary join. On the solid (red) lines within the main triangle two phases are present, which are the two located at both ends of each line: e.g., CCTO and TiO$_2$ are present on the line connecting CCTO (composition 1) and the TiO$_2$ corner. The various smaller secondary triangular regions within the main triangle all contain the three phases located in the corners of these triangles: e.g., CCTO, CTO and TiO$_2$ are present inside the triangle with corners CCTO, CTO and TiO$_2$.

Compositions 1–8 were chosen so that the volume concentration of potential secondary phases such as CuO, TiO$_2$ and CaTiO$_3$ would always be well below the percolation threshold for secondary phases randomly distributed within the primary CCTO matrix. This would ensure that the dielectric response in the sintered pellets of all of the labelled compositions would always be dominated by the CCTO phase. The theoretical percolation threshold for a secondary phase is known to be approximately 16%, whereas experimental values are commonly reported to be up to ≈ 20%.46

No direct evidence for two different CTO compositions is found in the phase diagram, i.e., for the GB and bulk CTO phases. The phase relationships detected are consistent with the notion that no major defect mechanism and related solid solution are directly obvious and that CTO and CCTO are the only non-trivial single phase compositions in agreement with recently published work.41 Therefore, the solid solutions potentially causing the non-stoichiometry listed above in eqn (A–E) would be small and are the green arrows in Fig. 1. For demonstration purposes the length of the (green) arrows is depicted as being much larger than the small extent to which the solid solutions would be expected to be developed.

Unclear results were obtained within the triangle with corners CuO, CTO and CaO, where the phase relationships could not be determined unambiguously. No signs of CaO and Ca$_2$CuO$_3$ were detected, in contrast to previous reports on 950 °C heat treated powders.41 The compositions in this triangle were prone to extensive partial melting of CuO and possibly Ca containing phases other than CaO and Ca$_2$CuO$_3$ were formed. In fact, none of the compositions investigated showed any sign of CaO formation. The XRD patterns and SEM micrographs for all of the numbered compositions (Fig. 1) are displayed in the ESL parts I(a) and (b).

The phase diagrams for the heat treatments at 1000 and 1100 °C were found to be identical, with one exception: no crystalline CuO phase could be detected at 1100 °C in any composition by powder XRD, whereas at 1000 °C crystalline CuO was detected in all compositions, where it was expected [see ESI, part I(a)]. It is suggested that CuO may partially melt at 1100 °C, which was confirmed in the CuO-rich pellets, where a Cu-rich phase precipitated out of the pellets during sintering at 1100 °C and remained on the Pt foil after cooling. No CuO phases could be detected in these pellets using XRD phase analysis, although some partially melted CuO may still be present in the GB areas and could remain amorphous or micro-crystalline after cooling and, therefore, cannot be detected by XRD.

The presence of a highly conductive Cu-rich phase was also confirmed on the surface of the pellet of composition 6 using C-AFM as presented in the ESI [part I(c)]. It should be mentioned that the proposed partial melting and precipitation process of CuO may also occur, to a smaller extent, during synthesis of CTO at 1000 °C. This may have prevented the full chemical reaction of CuO with the remaining precursors, which could serve as a plausible explanation for the unexpected finding of small amounts of CaTiO$_3$ in certain compositions (Table 1). In the case of such Cu deficiency and concomitant unexpected CaTiO$_3$ residues, some residual TiO$_2$ would be expected as well for stoichiometric reasons. In composition 1 no TiO$_2$ was detected, which may favour the mechanism in eqn (B) listed above or imply an unusual Ti-rich CaTiO$_3$ phase. All phases detected for the 1100 °C powders and their expected phase compositions are summarised in Table 1, together with all of the powder CCTO lattice parameters $a$ at 1100 and 1000 °C. It is evident that $a$ is generally larger for the samples heat treated at 1100 °C, possibly due to the partial reduction of cations and concomitant increase in the cationic radii, e.g., Ti$^{4+}$ → Ti$^{3+}$, or Cu$^{2+}$ → Cu$^+$. This finding may favour

<table>
<thead>
<tr>
<th>Compos. number</th>
<th>Cation ratio (fractions)</th>
<th>Expected phases (wt)</th>
<th>Detected phases (1100 °C)</th>
<th>$a/Å$ (1100 °C)</th>
<th>$a/Å$ (1000 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca 0.125, Cu 0.375, Ti 0.5</td>
<td>CCTO (1)</td>
<td>CCTO, [CTO]</td>
<td>7.3925 (1)</td>
<td>7.3916 (4)</td>
</tr>
<tr>
<td>2</td>
<td>Ca 0.11, Cu 0.33, Ti 0.56</td>
<td>CCTO (0.88), TiO$_2$ (0.12)</td>
<td>CCTO, TiO$_2$, [CTO]</td>
<td>7.3928 (1)</td>
<td>7.3917 (3)</td>
</tr>
<tr>
<td>3</td>
<td>Ca 0.14, Cu 0.3, Ti 0.36</td>
<td>CCTO (0.84), CTO (0.07), TiO$_2$ (0.09)</td>
<td>CCTO, CTO, TiO$_2$</td>
<td>7.3924 (3)</td>
<td>7.3905 (2)</td>
</tr>
<tr>
<td>4</td>
<td>Ca 0.175, Cu 0.325, Ti 0.5</td>
<td>CCTO (0.88), CTO (0.12)</td>
<td>CCTO, CTO, CuO</td>
<td>7.3931 (2)</td>
<td>7.3925 (3)</td>
</tr>
<tr>
<td>5</td>
<td>Ca 0.145, Cu 0.435, Ti 0.42</td>
<td>CCTO (0.74), CuO (0.17), CTO (0.09)</td>
<td>CCTO, CTO, CuO</td>
<td>7.3922 (2)</td>
<td>7.3929 (2)</td>
</tr>
<tr>
<td>6</td>
<td>Ca 0.1125, Cu 0.4375, Ti 0.45</td>
<td>CCTO (0.9), CuO (0.1)</td>
<td>CCTO, [CTO], CuO</td>
<td>7.3929 (4)</td>
<td>7.3911 (2)</td>
</tr>
<tr>
<td>7</td>
<td>Ca 0.1025, Cu 0.385, Ti 0.5125</td>
<td>CCTO (0.81), CuO (0.08), TiO$_2$ (0.11)</td>
<td>CCTO, TiO$_2$, [CTO], CuO</td>
<td>7.3915 (1)</td>
<td>7.3903 (2)</td>
</tr>
<tr>
<td>8</td>
<td>Ca 0.06, Cu 0.52, Ti 0.42</td>
<td>CCTO (0.47), CuO (0.35), TiO$_2$ (0.18)</td>
<td>CCTO, TiO$_2$, [CTO], CuO,</td>
<td>7.3912 (2)</td>
<td>7.3905 (3)</td>
</tr>
</tbody>
</table>
defect mechanisms involving high temperature cationic reduction, i.e., those in eqn (A) and (B).

For the 1100 °C fired powders it can be seen that the Cu containing compositions, 7 and 8, show smaller lattice parameters than compositions 1–6. This was regarded as an initial indication that the bulk CCTO may indeed exhibit Cu non-stoichiometry. However, the changes in lattice parameter for the different compositions are rather small (the maximum difference in the 1100 °C powders is 0.026%) and no conclusive trend between all of the other compositions is evident from their lattice parameters alone.

B. Impedance spectroscopy (IS)

Fig. 2 shows the IS data obtained from the 1100 °C sintered pellets of composition 1–8 at 80 K using the formalism of the real part of the dielectric permittivity, εʹ vs. the frequency, f (Fig. 2a), and the imaginary part of the electric modulus, Mʺ vs. f (Fig. 2b). The data have been fitted to the equivalent circuit model shown in Fig. 2a, which is discussed in more detail in section C. Fig. 2a displays two permittivity plateaus at high- and low-frequency as a result of the electronic heterogeneity of the pellets. This is well understood, for the single phase ceramic CCTO in terms of the typical IBLC structure.13 The low-frequency and high-permittivity plateau is interpreted as a GB effect and the high-frequency and low-permittivity plateau represents the intrinsic bulk.9 This interpretation requires that the brick-work layer model is valid and each relaxation can be described using a parallel resistor–capacitor element (RC element), and a possible equivalent circuit model would consist of a series of such RC elements.42,43 Fitting such a model to the data allows discrimination and separate analysis of the grain interior and GB dielectric response.

It is obvious from Fig. 2 that different secondary phases have a distinct influence on the dielectric behaviour and the IS data fall into two categories: Compositions 7 and 8 differ from 1–5, whereas 6 shows an intermediate dielectric response and may fall in between these two groups. According to the phase diagram in Fig. 1, compositions 7 and 8 belong to the same compositional triangle (CuO–CCTO–TiO₂), which would be a plausible explanation for their dielectric distinction. Below in section III(D) it will be shown that this interpretation is incomplete: compositions 5 and 6 also differ from 1–4 when their dielectric response is related to the CCTO lattice parameter a. It appears that it is in fact the presence or absence of the CuO secondary phase that separates the investigated compositions, according to their dielectric response, into two categories: i) 1, 2, 3, 4 (no extra CuO); and ii) 5, 6, 7 and 8 (with extra CuO). From Fig. 2a it can be seen that the low-frequency and high-permittivity plateau, which is associated with the GB permittivity, varies strongly with the composition. Such a variation may express changes in the GB composition and/or variation in the GB thickness. Discrimination between these two explanations is not possible, but a major influence from the grain size can be excluded. It is demonstrated in the ESI [part I(b)] that the grain size only slightly varies with changes in the composition.

The variations in the IBLC structure demonstrated in Fig. 2a for the different compositions will be analysed in detail in the following section in order to obtain information on potential defect mechanisms and solid solutions that are present. In several previous studies, the effect of secondary phases on the CCTO giant dielectric permittivity had been analysed in detail, but the giant permittivity is extrinsic in nature. Those analyses therefore gave phenomenological information only and the investigation of the intrinsic bulk dielectric relaxation was carried out in this work to gain fundamental insight into the potential intrinsic changes of the CCTO phase induced by the presence of different secondary phases.

For the analysis of the intrinsic bulk dielectric relaxation it is advantageous to display IS data in terms of the electric modulus formalism as plots of Mʺ vs. f (Fig. 2b). This is because each dielectric relaxation is shown as a relaxation peak in the Mʺ vs. f plots, where the relaxation with the smallest capacitance (bulk) exhibits the largest peak.42 In contrast, for the conventional impedance —Zʺ vs. f plot the dielectric relaxation peak for the relaxation with the largest resistance in the sample (GB) is the most pronounced.42 The
approximate peak frequencies for the GB and bulk relaxation peaks are given in eqn (1) for the respective plots of $-Z''$ vs. $f$ (GB) and $M''$ vs. $f$ (bulk), using two ideal RC elements connected in series. Eqn (1) implies that an extrinsic GB-type relaxation with large resistance and capacitance would appear at a lower $f$ than the bulk, which is a common feature in the experimental impedance spectra of electroceramics. The different ordinates of the GB and bulk relaxation peaks are shown in eqn (2) for a typical CCTO scenario with distinct differences between the GB and bulk RC elements.

$$\begin{align*}
 f_{\text{max}}(-Z'') &\approx \frac{1}{2\pi R_{\text{GB}} C_{\text{GB}}} = \frac{1}{2\pi \rho_{\text{GB}} \varepsilon_{\text{GB}} C_{\text{GB}}}; \\
 f_{\text{max}}(M'') &\approx \frac{1}{2\pi R_{\text{b}} C_{\text{b}}} = \frac{1}{2\pi \rho_{\text{b}} \varepsilon_{\text{b}} C_{\text{b}}}; \\
 -Z''(f_{\text{max}}) &\approx \frac{R_{\text{GB}}}{2} = \rho_{\text{GB}} \varepsilon_{\text{GB}}; \quad M''(f_{\text{max}}) \approx \frac{C_{\text{b}}}{2} = \frac{1}{2\varepsilon_{\text{b}}} \quad (2)
\end{align*}$$

$C_0$ and $\varepsilon_0$ represent the capacitance of the empty measuring cell in a vacuum and the dielectric permittivity of a vacuum, respectively. The geometrical factor $g$ is derived from the pellet surface $A$ divided by the pellet thickness $d$ ($g = A/d$). $R_{\text{GB}, C_{\text{GB}}}$ and $R_{\text{b}, C_{\text{b}}}$ represent the resistance and capacitance of the GB and bulk areas, respectively, whereas $\rho_{\text{GB}}$, $\varepsilon_{\text{GB}}$ and $\rho_{\text{b}}$, $\varepsilon_{\text{b}}$ correspond to the respective specific parameters of resistivity and dielectric permittivity. The differences in the peak ordinates in eqn (2) guarantee that for $-Z''$ vs. $f$ the relaxation peak representing the largest resistivity ($\rho_{\text{GB}}$) and for $M''$ vs. $f$ the peak representing the smallest permittivity ($\varepsilon_{\text{b}}$) are the most strongly pronounced.

$M''$ vs. $f$ data are plotted on double-logarithmic axes in Fig. 2b. For compositions 1–5 only one high $f$ relaxation peak is displayed, which is indicative of a conventional CCTO bulk dielectric relaxation process. Compositions 7 and 8 appear to display a flat peak response for $M''$ vs. $f$, but it is in fact a double peak response (see Fig. 2b, inset) and the bulk dielectric response seems to be distinctly different, whereas composition 6 falls in between these two types of responses. Again, as mentioned above, this interpretation is incomplete and the categories are divided into i) 1–4; and ii) 5–8. Notably, the impedance spectra of 7 and 8, as well as all of the other compositions, display two additional relaxation processes, GB and electrode contributions, which are not visible in Fig. 2a and b, but are at higher temperatures [ESI, part II(a) and (b)]. Therefore, neither of the double peaks in 7 and 8 are likely to represent a GB or electrode relaxation and may well be associated with two different bulk CCTO contributions or one CCTO contribution and a secondary phase. Since the typical high $f$ bulk dielectric relaxation peak displayed in compositions 1–5 is missing from 7 and 8, it may be plausible that the peak with the higher $f$ of the two double-peaks is more likely to represent the main bulk CCTO relaxation of composition 7 and 8. A complete absence of the CCTO bulk relaxation is unrealistic due to the XRD patterns clearly displaying the CCTO phase, which strongly dominates over all of the secondary phases.

Furthermore, it is important to consider that the double-peaks both occur at a significantly lower $f$ compared to the bulk peaks for compositions 1–5. If it is assumed that each relaxation can be described by an RC element, the height of the relaxation peaks in Fig. 2b would be proportional to the reciprocal dielectric permittivity $\varepsilon_b$ (eqn (2)), whereas the peak frequency is proportional to $R_b \times C_b$ or $\varepsilon_b \times \rho_b$ (see eqn (1)). This implies that the two processes in composition 7 and 8, represented by the two $M''$ vs. $f$ double-peaks, both exhibit significantly increased $\rho_b$ when compared to the single CCTO bulk relaxations for composition 1–5. The typical CCTO semiconducting bulk relaxation at high $f$ is missing. Therefore, $\rho_b$ must be strongly increased, because the typical low resistivity bulk CCTO relaxation process would be observable at high $f$, as in compositions 1–5, even in the presence of secondary phases, but no such observation was made. This was regarded as a further indication that the dielectric heterogeneity of CCTO is a result of the non-
stoichiometry of Cu. The relaxation peak of composition 6 indicates an increased resistivity, as well as being consistent with the presence of secondary phase CuO.

Due to strong relaxation peak broadening and overlap, the double peaks in composition 7 and 8 cannot be modelled using two bulk-type RC elements connected in series.

C. Equivalent circuit fitting

The impedance data from the 1100 °C sintered pellets of compositions 1–5 were fitted to the equivalent circuit model shown in Fig. 2a, which had been successfully applied before.44 Bulk and GB relaxations were represented by RC elements. The intrinsic bulk dielectric relaxation process was fitted to a standard RC element, i.e., an ideal resistor (R1) and capacitor (C1) in parallel and an additional constant-phase element (CPE) in parallel (CPE1). The use of such a CPE has been shown previously to be appropriate to account for non-ideal bulk relaxations in electroceramics.46 The extrinsic GB relaxation was fitted with a non-ideal RC element (R2–CPE2) where the ideal capacitor was replaced with a CPE (CPE2). Non-ideal R–CPE or R–CPE–C circuits indicate a broadening of the respective dielectric relaxation peak as a reflection of the broadening of the distribution of relaxation times, τ.47 In an ideal RC element τ is derived from: τ = RC = ρ0σe.

The two non-ideal RC elements were connected in series according to the brick-work layer model,45 and the data and model in Fig. 2a and b show good agreement. An equivalent circuit fit to composition 6 was also successfully carried out. The fitting errors were larger here, which may well be a reflection on the less ideal dielectric behaviour that was demonstrated in the M' vs. f plot (Fig. 2b).

The fitted bulk resistivity (ρb) and capacitance (εb) are plotted in Fig. 3a and b. The data could not be corrected for pellet porosity because the theoretical density was not accessible due to the mixed phase of the compositions and the potential Cu loss. Due to the high 1100 °C sintering temperature the pellet densities were assumed to be close to the theoretical value. In the case of composition 1, with a nominal single phase of CCTO, the experimental density was calculated to be 100%. In all other compositions CCTO is the major phase and CCTO grains were expected to sinter to a similarly high density. The ρb values are displayed as Arrhenius plots of logarithmic ρb vs. the reciprocal temperature 1000/T (Fig. 3a). All of the ln(ρb) vs. 1000/T curves show two distinct features: (1) a change in the general trend is evident near 80 K and conduction seems to undergo a transition; (2) differences between the various compositions are more distinct below 80 K.

It has been shown that at low temperatures (T ≤ 100 K) the electrical conduction in semiconductors is often dominated by impurities.48 The change of slope in all of the ln(ρb) vs. 1000/T curves may be explained by a transition into an impurity conduction regime upon cooling to T ≤ 80 K. Since the pellets all have different compositions it is plausible that conduction varies more strongly at T ≤ 80 K in the impurity conduction regime where additional phases may have a stronger impact. Above 80 K electrical conduction may be dominated by the bulk CCTO phase and, therefore, the curves for compositions 1–5 are similar. The trends in the ln(ρb) vs. 1000/T curves show only small quantitative differences for T > 80 K, whereas composition 6 deviates. Additional Cu increases the CCTO bulk resistivity as mentioned previously.

The capacitance C1 is shown as the plot of dielectric permittivity εb vs. T in Fig. 3b. It should be noted that the equivalent circuit component C1 represents the high-frequency, low-permittivity plateau, but it is not equal to the intrinsic bulk permittivity. C1 contains a small contribution from the GB permittivity and can be corrected accordingly. This correction procedure has been carried out successfully on the IS data for Sr-doped CCTO,10 but it was found here that such a correction would change εb only marginally below the experimental error and equivalent circuit fitting errors. The sintering temperature (1100 °C) was higher here compared to the 1000 °C used in ref. 10, which led to a much more pronounced IBLC structure. As a consequence, we find larger differences between the GB and bulk permittivity and the GB permittivity has only a marginal effect on the bulk value. In Fig. 3b the uncorrected εb values are shown.

The apparent increase of εb (Fig. 3b) with reducing temperature can be explained either by incipient ferroelectric...
tricity or a charge-transfer mechanism. Such behaviour in CCTO has been reported previously, and is confirmed here. All of the trends in the $\varepsilon_b$ vs. $T$ curves are qualitatively similar and only quantitative variations are evident. Such quantitative differences are difficult to interpret from Fig. 3b alone. In the next section it will be demonstrated that such differences are correlated with the CCTO lattice parameter $a$.

D. Combined analysis of lattice and dielectric parameters

Summarising the results from the above section, indications have been found in the impedance spectra that the potential non-stoichiometry in CCTO may involve Cu. In this section clear trends between the bulk resistivity $\rho_b$ vs. lattice parameter $a$ and bulk dielectric permittivity $\varepsilon_b$ vs. $a$ are presented and at least two different defect mechanisms and associated solid solutions in CCTO are revealed.

i) Cu-deficient compositions. Fig. 4a shows a plot of bulk resistivity $\rho_b$ for compositions 1–6 (obtained from equivalent circuit fits) vs. the lattice parameter $a$ (determined from high resolution powder XRD). For compositions 1–4, $\rho_b$ at 150 K shows a modest and approximately linear increase with $a$. It is unclear at this point whether this increase of $\rho_b$ with $a$ represents a solid solution, because the increase is small and may simply be a consequence of the increasing atomic distance of the cations. With increasing $a$ the orbital overlap may reduce leading to higher $\rho_b$.

Compositions 5 and 6 do not follow the same trend and their $\rho_b$ values seem to be elevated. The curves of $\rho_b$ vs. $a$ for compositions 1–6 at alternative temperatures of 20, 50 and 100 K all show equivalent features. This confirms that the presence of extra Cu in 5 and 6 leads to a higher bulk $\rho_b$ compared to compositions 1–4. The highly resistive GB regions may contain a higher Cu content than the semiconducting Cu-deficient bulk.

The trend for the dielectric permittivity, $\varepsilon_b$, obtained from the equivalent circuit fits vs. $a$ is presented in Fig. 4b, where the dielectric data have been collected at 100 K. The main feature of this data is the increase in dielectric permittivity $\varepsilon_b$ with $a$ for compositions 1–4, which cannot be explained by a simple lattice expansion. The Clausius–Mossotti equation predicts an approximately constant $\varepsilon_b \approx 48$, taking into consideration the small changes in $a$ observed and the atom polarizabilities obtained from ref. 19. The secondary phases in compositions 1–4, CaTiO$_3$ and/or TiO$_2$, both have a lower permittivity than CCTO and, therefore, cannot cause such an anomalous increase in $\varepsilon_b$ directly, but may well influence the defect mechanism in the CCTO bulk phase responsible for the $\varepsilon_b$ increase to $\approx 100$. If it were the case that the secondary phase of CuO simply extends the existing defect mechanism for compositions 1–4 to higher Cu contents, compositions 5 and 6 would be expected to fall onto the same line as 1–4, which is clearly not the case, therefore, one or more additional defect mechanisms may well exist. The mechanism detected for compositions 1–4 may not involve large differences in Cu content because, in this case, a larger variation of $\rho_b$ with $a$ than that detected in Fig. 4a would be expected. Additionally, significant changes in the oxygen content are unlikely, because the concomitant changes in cationic valence would also be expected to lead to larger variations in $\rho_b$.

ii) Cu-rich compositions. To elucidate the role of the secondary CuO phase on the CCTO bulk resistance, $\rho_b$ values for all compositions containing extra CuO (5–8) were estimated from the relaxation peak height and peak position in the $\varepsilon'$ vs. $f$ plots (Fig. 2b) according to eqn (1) and (2).

For the double-peaks in compositions 7 and 8 estimates were taken from the peak at a higher $f$ in the $\varepsilon'$ vs. $f$ plots, which was argued above to be more likely to represent the main CCTO bulk relaxation. The estimated $\rho_b$ values obtained from the $\varepsilon'$ vs. $f$ plots for compositions 5 and 6 were compared to the respective $\rho_b$ values from the equivalent circuit fits [see section III(C)]. It was found that at 80 K the estimated $\rho_b$ values were smaller by a factor of 3.3 (composition 5) and 3.7 (composition 6) than the values from the equivalent circuit fits. This can be explained by the non-ideality of the relaxation processes leading to a broadening of the relaxation peaks in $\varepsilon'$ vs. $f$. This, in turn, leads to a reduction in peak height and an overestimate of $\varepsilon_b$ according to eqn (2). The error made in the estimation of $\rho_b$ from the $\varepsilon'$ vs. $f$ plots was approximated to be a uniform factor of $\approx 3.5$. Thus, the estimated values (■ in Fig. 5) for compositions 7 and 8 were multiplied by a factor of 3.5 in order to account for the estimation error. Both, the uncorrected (□) and corrected (■)$\rho_b$ values for compositions 7 and 8 at 80 K are plotted vs. $a$ in Fig. 5 and approximately fall onto one line with composition 5 displaying a significant increase in $\rho$ with decreasing $a$. Composition 6 is an exception to this trend, which is probably an experimental error or artefact. Still, the significant $\rho_b$ increase with decreasing $a$ detected in the Cu-rich samples 5, 7 and 8 strongly suggests the existence of a second defect mechanism and an associated solid solution. This mechanism may well relate the large differences between the GB and bulk resistivity to the Cu concentration: the GB regions would be Cu-rich and bulk regions Cu-deficient. Or, in other terms, the GB regions would exhibit compositions with a higher Cu-

![Graph showing trends](image-url)
content, possibly quite close to the stoichiometric and nominally insulating CCTO phase, in contrast to the Cu-deficient bulk. The defect mechanisms mentioned above in eqn (B–D) involve Cu deficiency, but from the data presented here a clear discrimination is difficult. In agreement with the indications mentioned above, the mechanisms in eqn (B) and (C) may be favourable though, because the increase in \( a \) with decreasing \( \rho_b \) for the Cu-rich compositions (5–8), displayed in Fig. 5, may be inconsistent with the mechanism in eqn (D).

IV. Summary and discussion

Combined analysis of the XRD lattice parameter \( a \) and IS data revealed approximately linear relationships between the CCTO bulk resistivity \( \rho_b \) vs. \( a \) and the intrinsic bulk dielectric permittivity \( \varepsilon_b \) vs. \( a \). For Cu-deficient compositions 1–4, an anomalous increase of the CCTO bulk dielectric permittivity \( \varepsilon_b \) with \( a \) was found, above that predicted using the Clausius–Mossotti equation, as a result of a distinct defect mechanism.

Compositions 5–8 containing a CuO secondary phase did not follow the same trends. The presence of excess CuO led to an increased \( \rho_b \) and indications of a second defect mechanism were found, which may explain the large difference between the GB and bulk resistivity in terms of the difference in Cu content. This would most likely be associated with the defect mechanisms in eqn (B) and (C), mentioned in section I. For compositions 1–4 the source of their semiconductivity in the respective CCTO bulk phase may also be due to Cu deficiency, but it may be independent of the TiO\(_2\) and/or CaTiO\(_3\) secondary phases since no large differences in \( \rho_b \) were detected.

The rather small increase of \( \rho_b \) with \( a \) in compositions 1–4 (Fig. 5a) leads to some further important conclusions: the underlying defect mechanism causing high \( \varepsilon_b \) may not involve any large changes in the cationic valence of Cu and/or Ti, in which case larger differences in \( \rho_b \) would be likely. This would exclude major contributions from all of the mechanisms mentioned above in eqn (A–D), except for the mechanism shown in eqn (E), which concerns a Cu excess compensated for by the formation of oxygen vacancies. Since compositions 1–4 are all Cu-deficient, the mechanism in eqn (E) is unlikely. Instead, the formation of anti-site defects like Ca–Cu, Cu–Ti or Ca–Ti inter-site cation exchanges may be a more plausible explanation. Evidence for Ca–Cu anti-site disorder has indeed been reported in the literature, although it should be noted that, in this work, the Ca–Cu anti-site defects are proposed to serve as an explanation for the increased bulk permittivity \( \varepsilon_b \) and not for the extrinsic giant permittivity \( \varepsilon_{\text{GB}} \).

The trends seen in \( \rho_b \) vs. \( a \) and \( \varepsilon_b \) vs. \( a \) are relatively uniform for all of the compositions investigated, which may be a result of the identical powder synthesis and pellet sintering conditions employed. The two distinct defect mechanisms detected were only obvious from combined analysis of \( a \) and the IS data, and cannot be clearly identified otherwise. From the difficulty of detection it is obvious that the extent to which the defect mechanisms in CCTO ceramics are developed may be small and difficult to control.

V. Conclusions

Compositions in the CaO–CuO–TiO\(_2\) phase triangle without a CuO secondary phase exhibit an anomalous increase of the CCTO bulk dielectric permittivity \( \varepsilon_b \) with \( a \) above the values predicted from the Clausius–Mossotti equation. This was associated with a defect mechanism based on Ca–Cu anti-site defects, which causes a high intrinsic bulk dielectric permittivity. Compositions containing a CuO secondary phase exhibit increased resistivity. A second mechanism is proposed to be responsible for the large difference between the GB and bulk resistivity in CCTO: GB areas may be Cu-rich, whereas bulk areas may be Cu-deficient. Such Cu gradients may well develop during the ceramic sintering processes.

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