Tunable dielectric properties of niobium (Nb) doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocubes synthesized via facile molten salt route

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Abstract

Doping induced tuning of dielectric constant of nanomaterials has huge technological importance, but its realization is limited by lack of synthetic protocols for uniform dielectric nanostructures, with controlled doping. Here, nanocubes of niobium doped calcium copper titanate (Nb-doped CCTO) is realized through molten salt route and the effect of Nb doping on tunability of dielectric behavior is reported. Particular focus is to minimize the significant dielectric loss which is practical concern of CCTO based giant dielectric materials. The structural and compositional properties of as synthesized powders and sintered pellets are analyzed by X-ray diffraction, field emission scanning electron microscopy and energy dispersive X-ray spectroscopy. XRD analysis carried out on the samples confirmed single phase formation and indicated overall increase in lattice constant. The surface morphology of the molten salt derived product shows nanocubes with size in the range of 250–280 nm. Energy dispersive X-ray spectroscopy pattern confirmed the presence of Nb in doped samples. The dielectric response of sintered $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ samples studied by precision LCR meter suggest that although Nb substitution in CCTO reduces the dielectric constant but dielectric loss had lower values than those of undoped CCTO.

Keywords Dielectric materials · Molten salt · Nanostructure · X-ray diffraction

1 Introduction

For the past few decades, lead-free electroceramics with giant dielectric constant and good thermal stability has particularly enticed attention for their practical applications in miniaturizing microelectronic devices. Recently, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (hereafter CCTO), a body-centered cubic perovskite-related structure (space group $\text{Im}\bar{3}$, lattice parameter of 7.391 Å) has grown significant consideration because of its stunning relative dielectric constant ($\epsilon_r \sim 10^3$ – 10^5) at room temperature (RT). Furthermore, the dielectric constant is found to be almost frequency independent from dc to 1 MHz with little temperature dependence in a broad temperature range from 100 to 400 K [1, 2], making it a favorable candidate for many important applications [3–9]. However, the dielectric loss ($\tan \delta$) of CCTO is relatively high (0.1 at 1 kHz at RT) making it inapt

for device fabrication. Various explanations have been specified to understand the origin of colossal dielectric constant in CCTO ceramics [1, 2, 10–12]. Till date, internal barrier layer capacitance (IBLC) mechanism [10] is widely accepted for explaining the origin of high value of dielectric constant shown by CCTO ceramics. Literature survey reveals that microstructural and dielectric properties of CCTO strongly depends on different processing routes [13–20] and preparation conditions such as sintering temperature and time [21–24], contact-electrode effect [25–27] and so on. In recent years, various new processing techniques [20, 28–30] have also been employed to obtain CCTO in the nanocrystalline form, thereby depressing the processing temperature and time without compromising on its properties. The processing time in these methods ranges from several minutes to few hours.

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Molten salt synthesis (MSS) [31–36] has been reported to be one of the simplest route to prepare nanoparticle, ceramic materials as well as carbon based materials at lower temperatures and often in overall shorter reaction times with tiny residual impurities. This method is centered on the use of different types of inorganic salt or salt mixture providing a liquid reaction environment thereby quickening the crystal growth. Previous attempts at synthesizing CCTO by MSS route [37, 38] resulted in non-phase pure agglomerated sub-micron or micron-sized particles with no specific morphology. Compared to nanoparticles of CCTO as frequently reported [28–30], synthesis protocol for one dimensional nanostructure of doped CCTO is still a major challenge. Although the dielectric properties of the Nb-doped CCTO ceramics have been reported earlier [39–41], the synthesis of Nb-doped CCTO nanostructure by MSS route have never been reported.

In this work, phase pure, crystalline Nb-doped CCTO nanostructures with well-defined shape has been synthesized for the first time by molten salt route using NaCl–KCl eutectic mixtures. The study reveals that substitution of Nb has remarkable influence on both the microstructure and dielectric response in CCTO.

2 Experimental details

Nb-doped CCTO nanocubes are prepared using a simple molten salt synthetic method. All materials are purchased from commercial sources (analytical grade) and used without further purification. Calcium acetate (Merck, India), copper acetate (Merck, India), niobium pentoxide (Merck, India) and titanium dioxide (anatase, Sigma Aldrich) are taken as starting raw materials while NaCl–KCl salt mixture (1:1 molar ratio, m.p.: 657 °C) is used as molten salt. The starting raw materials, taken in stoichiometric amount according to $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ ($x = 0, 0.05, 0.1$) and salts are mixed in a molar ratio of 1:3:4:40:40 in a agate mortar and hand grinded for 30 min. The mixtures are transferred to a high purity alumina crucible and calcined in a box furnace at 850 °C 2 h in air with a heating rate of 4 °C/min. After natural cooling of furnace to room temperature, the reacted mass are collected and washed several times with ample amount of distilled water. The resultant products are finally oven dried at 60 °C overnight before characterization.

The phases and crystallinity of the as-prepared powders are identified by powder X-ray diffractometer (XRD, Bruker, D-8 Advance) using Cu K α radiation of wavelength $\lambda = 1.5406$ Å. The size distributions and morphologies of the as washed powder and sintered pellets are observed using a field emission scanning electron microscope

(FESEM, S-4800, Hitachi, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS).

In order to measure the dielectric properties, the obtained powders are pressed under 5 MPa pressure to form disk of 1 mm thickness and 10 mm in diameter. The brown disk is sintered at 1000 °C for 5 h in the air. The sintered samples are polished to produce a flat uniform surface and fine copper leads are electroded by silver paste and heat treated at 150 °C for 15 min prior to electrical measurement. The dielectric response of the sintered samples are recorded using a computer controlled Precision LCR Meter (Agilent E4980A) over a broad frequency range (20 Hz–1 MHz) at different temperatures (30–220 °C).

3 Results and discussion

3.1 XRD analysis

Figure 1 shows the XRD patterns of $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ powders with different Nb⁵⁺ doping concentrations. All the diffraction peaks appeared in the patterns are matched

Fig. 1 **a** XRD patterns of pure and Nb doped CCTO synthesized at 850 °C for 2 h, **b** lattice parameter as a function of Nb substitution

with the peaks of the pseudo-cubic CCTO by comparing with the standard powder diffraction file database [JCPDS-75-2188]. Formation of single phase up to $x=0.1$ Nb-substitution is confirmed by absence of the characteristic lines of constituent oxides or the other phases in the powder X-ray diffraction patterns in all as synthesized powders. The lattice constant increases linearly with Nb-substitution and it becomes 7.396 Å at $x=0.1$ Nb-substitution. The increased lattice constant can be attributed to the ionic radius and valence differences between Ti and Nb ions ($r(\text{Ti}^{4+})=0.605$ Å and $r(\text{Nb}^{5+})=0.64$ Å) [42].

3.2 FESEM analysis

Figure 2 shows the FESEM images of pure and Nb-doped CCTO nanostructures prepared at 850 °C for 2 h. It can be seen that all the products are mainly composed of distinct nanocubes with few irregular aggregates. Cube size of undoped sample as estimated from Fig. 2a are in the range 250–280 nm. However, with increasing doping concentration, morphologies of cubic particles are not uniform (Fig. 2b, c) and cube size is found to decrease slightly (~ 200 nm for $x=0.1$ sample) with a corresponding

increase in aggregation and clumping in nanocubes. The reason for this aggregation is that when the doping concentration is high, the growth of particle is too fast to form the uniform intrinsic cubic shape.

Energy dispersive X-ray (EDX) analysis of as prepared $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ ($x=0.05$) nanocube synthesized at 850 °C for 2 h is shown in Fig. 2d. The presence of peaks of Ca, Cu, Ti, Nb and O with their respective band energies and the absence of any impurity peaks in the EDS spectrum prove the elemental and phase purity of the as prepared $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ nanocube. The elemental composition (atomic percentage) of $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ for $x=0, 0.05$ and 0.10 are given in Table 1.

3.3 Dielectric properties of sintered pellets

Figure 3a–c shows FESEM images of the surface morphologies of the Nb-doped CCTO ceramics sintered at 1000 °C for 5 h. The morphology of the undoped sample (Fig. 3a) is represented by fine-grained microstructure with grain sizes of about 10–15 μm with few smaller grains and holes. A decrease of the average grain size (~ 5 μm) is observed in the $x=0.05$ doped sample (Fig. 3b). This sample has a

Fig. 2 FESEM images of Nb-doped CCTO nanostructures synthesized at 850 °C for 2 h **a** $x=0$, **b** $x=0.05$, **c** $x=0.1$ and **d** EDS spectrum of $x=0.05$ sample

Table 1 Elemental composition (atomic percentage) of $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ for $x=0, 0.05$ and 0.10

Sample	CaK	CuK	TiK	OK	NbL
$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$	4.32	12.64	18.74	64.30	–
$\text{CaCu}_3\text{Ti}_{3.95}\text{Nb}_{0.05}\text{O}_{12}$	4.01	12.70	17.01	66.15	0.13
$\text{CaCu}_3\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_{12}$	3.36	10.98	15.74	69.51	0.41

Fig. 3 FESEM images of Nb-doped CCTO pellets sintered at 1000°C for 5 h **a** $x=0$, **b** $x=0.05$, **c** $x=0.1$

microstructure consisting of some large grains ($5\text{--}8\ \mu\text{m}$), surrounded by smaller ones ($< 1\ \mu\text{m}$). The surfaces of the samples doped with $x=0.10$ (Fig. 3c) is characterized by loosely packed grains with sizes lying between 1 and $2\ \mu\text{m}$. From the microstructural observation, it is clear that the increasing Nb concentration has changed the size and shape of particles from cubic to polyhedral dimensions during sintering.

It is well known that dielectric property of the ceramic is related firmly to its microstructure. The evolution of the microstructure with increasing Nb doping concentration is also reflected in the dielectric properties of the ceramic. Figure 4a and b shows the frequency dependence of the dielectric constant (ϵ_r) and the loss tangent ($\tan \delta$) of sintered pellets for the pure and Nb-doped CCTO at RT (30°C) (We could not measure the dielectric property of samples without sintering because the samples were otherwise too porous). As can be seen from Fig. 4a, all the samples show giant dielectric constant ($\epsilon_r \sim 750\text{--}1000$) in broad frequency ranges. It can be seen that the value of ϵ_r of pure sample first decreases rapidly in lower-frequency range ($100\ \text{Hz}\text{--}1\ \text{kHz}$), then decreases slowly in the mid frequency range ($1\ \text{kHz}\text{--}100\ \text{kHz}$) and then a sharp decline of ϵ_r is observed beyond $100\ \text{kHz}$ which is a typical characteristic of Debye relaxation and is consistent with reported result of CCTO [43]. However, the value of ϵ_r of Nb doped CCTO ceramic decreases gradually from a very high magnitude in lower frequency range below $1\ \text{kHz}$ and then remains almost constant from $1\ \text{kHz}$ to $1\ \text{MHz}$ whereas no such drastic decrease in ϵ_r at high frequency ($> 100\ \text{kHz}$) is observed for the doped samples. The high ϵ_r at low frequency is due to interfacial space charge polarization [44] which arises due to accumulation of charge carriers at the interface of semiconducting grains and insulating grain boundary. The RT values of ϵ_r at $1\ \text{kHz}$, $10\ \text{kHz}$, $100\ \text{kHz}$ for the $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ samples are summarized in Table 2. Obviously, ϵ_r decreases with increasing Nb doping concentration and this decline is consistent with decreasing mean grain size as evident from FESEM analysis of sintered pellets. According to the internal barrier layer capacitor (IBLC) model [10–12, 21], the effective dielectric constant (ϵ_{eff}) of a polycrystalline ceramic can be described as

$$\epsilon_{\text{eff}} = \frac{t\epsilon_{\text{gb}}}{t_{\text{gb}}} \quad (1)$$

where t , ϵ_{gb} and t_{gb} are the average grain size, dielectric constant of the GB and the thickness of GB respectively. Therefore, the change in dielectric properties of the Nb doped CCTO ceramics can be correlated to microscopic changes in microstructure of ceramics, i.e., decline of ϵ_r is primarily attributed to decrease in average grain size. Such dielectric behavior is similar to that observed in pure and

Fig. 4 Frequency dependence of **a** dielectric constant (ϵ_r) and **b** dielectric loss ($\tan \delta$) of Nb-doped CCTO pellet at room temperature, **c** temperature dependence of ϵ_r of the sintered pellets at 1 kHz

Table 2 The RT values of ϵ_r and $\tan \delta$ (at 1 kHz, 100 kHz, 100 kHz) for the $\text{CaCu}_3\text{Ti}_{4-x}\text{Nb}_x\text{O}_{12}$ sample

Sample	At 1 kHz		At 10 kHz		At 100 kHz	
	ϵ_r	$\tan \delta$	ϵ_r	$\tan \delta$	ϵ_r	$\tan \delta$
$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$	4145	0.41	3050	0.26	1653	0.64
$\text{CaCu}_3\text{Ti}_{3.95}\text{Nb}_{0.05}\text{O}_{12}$	890	0.35	754	0.09	680	0.07
$\text{CaCu}_3\text{Ti}_{3.9}\text{Nb}_{0.1}\text{O}_{12}$	650	0.22	490	0.13	448	0.10

doped CCTO ceramics [40, 45–49]. But, these results indicate that Nb substitution in Ti site of CCTO have not only an impact on its microstructure, but also pointedly affect its dielectric properties.

The striking effect of the Nb-substitution comes from the decrease of $\tan \delta$. As can be seen in Fig. 4b, $\tan \delta$ decreases initially, reaches minimum and then increases with increasing frequency. The increase in $\tan \delta$ in high frequency range for all samples is ordinarily related to dielectric relaxation process and high value of $\tan \delta$ in low-frequency range is usually associated with dc conduction processes [50, 51]. At $x=0.05$, this effect is rather remarkable. Compared back with the parent CCTO sample, the $\tan \delta$ of the $x=0.05$ sample is reduced by 3 to 9 times at higher frequencies. Combining Fig. 4a, b, the lowest dielectric loss is obtained at $x=0.05$ and ϵ_r shows better frequency stability from 1 kHz to 1 MHz and may have potential for capacitor application at high frequencies.

The variation of ϵ_r in the temperature range from 30 to 220 $^{\circ}\text{C}$ (at 1 kHz) for all the samples is demonstrated in Fig. 4c. It is observed that for undoped CCTO, ϵ_r is nearly temperature independent up to 100 $^{\circ}\text{C}$ whereas Nb-substituted samples have the temperature-independent ϵ_r up to 135 $^{\circ}\text{C}$.

To recognize the effect of Nb^{5+} doping on $\tan \delta$ values of CCTO ceramics, the electrical properties of grains and grain boundaries (GBs) are investigated using complex impedance plot (Z^*) at RT (Fig. 5). Although the completed semicircular arcs of all the samples can't be observed in the measured frequency range at RT, the effect of Nb substitution on the electrical response of GBs is clearly visible. As can be seen, the resistance of grain boundary reaches the highest value of 24.57 M Ω for $x=0.05$, which results in the lowest dielectric loss and signifies that low dielectric loss is associated with high resistivity for the dielectric material. Thus, the decrease in $\tan \delta$ for Nb-doped CCTO ceramics is attributed to the increase of R_{gb} . From all these findings, it can be concluded that MSS method is an effective way to improve the dielectric properties of CCTO and appropriate amount of Nb^{5+} substitution on Ti site of CCTO can lower the $\tan \delta$ which is favorable for practical application.

Fig. 5 Room temperature Complex impedance (Z^*) plot of Nb doped CCTO ceramics; inset shows the Z^* plot of undoped CCTO

4 Conclusion

In summary, Nb-doped CCTO nanocubes have been prepared with a novel and simple one-step molten salt method and their microstructures and dielectric properties are investigated. The microstructural analysis reveals that the mean grain size tends to decrease with increasing Nb doping content. Dielectric constant of sintered pellets are observed to be decreased with increasing Nb-substitution whereas doped samples show lower dielectric loss in the measured frequency range. Negligible variation of ϵ_r of doped samples in the temperature range of 35–140 °C at higher frequency (10 kHz or 100 kHz) with reduced dielectric loss makes these materials well suited for device fabrication. Impedance spectrum analysis confirms that reduced dielectric loss is associated with high grain boundary (R_{gb}) resistivity for the dielectric material. Because of the simplicity and generalizability of the approach used, it is expected that this methodology can be expanded to the large-scale synthesis (gram quantity) of other important multicomponent dielectric materials at the nanoscale.

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Compliance with ethical standards

Conflict of interest The author states that there is no conflict of interest.

References

- Homes CC, Vogt T, Shapiro SM, Wakimoto S, Ramirez AP (2001) Optical response of high dielectric constant perovskite related oxide. *Science* 293:673–676
- Subramanian MA, Li D, Duan N, Reisner BA, Sleight AW (2000) High dielectric constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ phases. *J Solid State Chem* 151:323–3253
- Chung SY, Kim ID, Kang SJL (2004) Strong nonlinear current–voltage behaviour in perovskite-derivative calcium copper titanate. *Nat Mater* 3:774–778
- Kim ID, Rothschild A, Hyodo T, Tuller HL (2006) Microsphere templating as means of enhancing surface activity and gas sensitivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films. *Nano Lett* 6:193–198
- Parra R, Savu R, Ramajo LA, Ponce MA, Varela JA, Castro MS, Bueno PR, Joanni E (2010) Sol–gel synthesis of mesoporous $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films and their gas sensing response. *J Solid State Chem* 183:1209–1214
- Kretly CL, Almeida AFL, Fachine PBA, Oliveira RSD, Sombra ASB (2004) Dielectric permittivity and loss of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) substrates for microwave devices and antennas. *J Mater Sci Mater Electron* 15:657–663
- Li M, Chen XL, Zhang DF, Wang WY, Wang WJ (2010) Humidity sensitive properties of pure and Mg-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Sens Actuators B* 147:447–452
- Pandey RK, Stapleton WA, Tate J, Bandyopadhyay AK, Sutanto I, Sprissler S, Lin S (2013) Applications of CCTO supercapacitor in energy storage and electronics. *AIP Adv* 3:062126
- Clark JH, Dyer MS, Palgrave RG, Ireland CP, Darwen JR, Claridge JB, Rosseinsky MJ (2011) Visible light photo-oxidation of model pollutants using $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: an experimental and theoretical study of optical properties, electronic structure, and selectivity. *J Am Chem Soc* 133:1016–1032
- Sinclair DC, Adams TB, Morrison FD, West AR (2002) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: one-step internal barrier layer capacitor. *Appl Phys Lett* 80:2153–2155
- Adams TB, Sinclair DC, West AR (2002) Giant barrier layer capacitance effects in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *Adv Mater* 14:1321–1323
- Lunkenheimer P, Fichtl R, Ebbinghaus SG, Loidl A (2004) Nonintrinsic origin of the colossal dielectric constants in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Phys Rev B* 70:172102
- Liu J, Smith RW, Mei WN (2007) Synthesis of the giant dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by wet-chemistry methods. *Chem Mater* 19:6020–6024
- Jha P, Arora P, Ganguli AK (2003) Polymeric citrate precursor route to the synthesis of the high dielectric constant oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Mater Lett* 57:2443–2446
- Barbier B, Combettes C, Fritsch SG, Chartier T, Rossignol F, Rumeau A, Lebey T, Dutarde E (2009) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics from co-precipitation method: dielectric properties of pellets and thick films. *J Eur Ceram Soc* 29:731–735
- Yu H, Liu H, Luo D, Cao M (2008) Microwave synthesis of high dielectric constant $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J Mater Process Technol* 208:145–148
- Sen A, Maiti UN, Maiti S, Chattopadhyay KK (2013) Single crystalline nanostructures of giant dielectric calcium copper titanate: a convenient route toward materialization of hard to realize multi-component perovskite nanostructures. *J Mater Science* 48:3967–3974
- Prakash BS, Varma KBR (2008) Molten salt synthesis of nanocrystalline phase of high dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J Nanosci Nanotechnol* 8:5762–5769
- Liu J, Sui Y, Duan C, Mei WN, Smith RW, Hardy JR (2006) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: low-temperature synthesis by pyrolysis of an organic solution. *Chem Mater* 18:3878–3882

20. Kumar R, Zulfequar M, Sharma L, Singh VN, Senguttuvan TD (2015) Growth of nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic by the microwave flash combustion method: structural and impedance spectroscopic studies. *Cryst Growth Des* 15:1374–1379
21. Adams TB, Sinclair DC, West AR (2006) Influence of processing conditions on the electrical properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *J Am Ceram Soc* 89:3129–3135
22. Ni WQ, Zheng H, Yu JC (2007) Sintering effects on structure and dielectric properties of dielectrics $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J Mater Sci* 42:1037–1041
23. Prakash BS, Varma KBR (2008) Effect of sintering conditions on the microstructural, dielectric, ferroelectric and varistor properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{La}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics belonging to the high and low dielectric constant members of $\text{ACu}_3\text{M}_4\text{O}_{12}$ (A = alkali, alkaline-earth metal, rare-earth metal or vacancy, M = transition metal) family of oxides. *Phys B Condens Matter* 403:2246–2254
24. Schmidt R, Stennett MC, Hyatt NC, Pokorny J, Prado-Gonjal J, Li M, Sinclair DC (2012) Effects of sintering temperature on the internal barrier layer capacitor (IBLC) structure in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics. *J Eur Ceram Soc* 32:3313–3323
25. Li M, Shen ZJ, Nygren M, Feteira A, Sinclair DC, West AR (2009) Origin(s) of the apparent high permittivity in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics: clarification on the contributions from internal barrier layer capacitor and sample-electrode contact effects. *J Appl Phys* 106:104106
26. Li M, Zhang DF, Wang WY, Wang G, Chen XL (2010) The effect of grain boundary response and electrode contact response on the dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J Phys D Appl Phys* 43:295405
27. Yang J, Shen M, Fang L (2005) The electrode/sample contact effects on the dielectric properties of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic. *Mater Lett* 59:3990–3993
28. Banerjee N, Krupanidhi SB (2010) Low temperature synthesis of nano-crystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ through a fuel mediated autocombustion pathway. *Curr Nanosci* 6:432–438
29. Jesurani S, Kanagesan S, Velmurugan SR, Thirupathi C, Sivakumar M, Kalaivani T (2011) Nanoparticles of the giant dielectric material, calcium copper titanate from a sol–gel technique. *Mater Lett* 65:3305–3308
30. Masingboon C, Maensiri S, Yamwong T, Anderson PL, Seraphin S (2008) Nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders prepared by egg white solution route: synthesis, characterization and its giant dielectric properties. *Appl Phys A* 91:87–95
31. Xing X, Zhang C, Qiao L, Liu G, Meng J (2006) Facile preparation of ZnTiO_3 ceramic powders in sodium/potassium chloride melts. *J Am Ceram Soc* 89:1150–1152
32. Mao Y, Banerjee S, Wong SS (2003) Large-scale synthesis of single-crystalline perovskite nanostructures. *J Am Ceram Soc* 125:15718–15719
33. Arendt RH (1973) The molten salt synthesis of single magnetic domain $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ crystals. *J Solid State Chem* 8:339–347
34. Liu XF, Fechner N, Antonietti M, Willinger MG, Schlögl R (2016) Synthesis of novel 2-d carbon materials: sp^2 carbon nanoribbon packing to form well-defined nanosheets. *Mater Horiz* 3:214–219
35. Liu XF, Fechner N, Antonietti M (2013) Salt melt synthesis of ceramics, semiconductors and carbon nanostructures. *Chem Soc Rev* 42:8237–8265
36. Liu XF, Antonietti M (2013) Moderating black powder chemistry for the synthesis of doped and highly porous graphene nanoplatelets and their use in electrocatalysis. *Adv Mater* 25:6284–6290
37. Chen K, He Y, Liu D, Liu Z (2008) Molten salt synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Key Eng Mater* 368–372:115–117
38. Prakash BS, Varma KBR (2008) Molten salt synthesis of nanocrystalline phase of high dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *J Nanosci Nanotechnol* 8:5762–5769
39. Hong SH, Kim DY, Park HM, Kim YM (2007) Electric and dielectric properties of Nb-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *J Am Ceram Soc* 90:2118–2121
40. Liu P, He Y, Zhou JP, Mu CH, Zhang HW (2009) Dielectric relaxation and giant dielectric constant of Nb-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics under dc bias voltage. *Phys Status Solidi A* 206:562–566
41. Sulaiman MA, Hutagalung SD, Mohamed JJ, Ahmad ZA, Ain MF, Ismail B (2011) High frequency response to the impedance complex properties of Nb-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ electroceramics. *J Alloys Compd* 509:5701–5707
42. Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst A* 32:751–767
43. Liu J, Duan C-g, Mei WN, Smith RW, Hardy JR (2005) Dielectric properties and Maxwell–Wagner relaxation of compounds $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ (A = Ca, $\text{Bi}_{2/3}$, $\text{Y}_{2/3}$, $\text{La}_{2/3}$). *J Appl Phys* 98:093703
44. Singh A, Mursalin SM, Rana P, Sen S (2015) Electrical properties of palladium-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *Appl Phys A* 120:1011–1021
45. Thongbai P, Putasaeng B, Yamwong T, Maensiri S (2012) Current–voltage nonlinear and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared by a simple thermal decomposition method. *J Mater Sci Mater Electron* 23:795–801
46. Adams TB, Sinclair DC, West AR (2006) Characterization of grain boundary impedances in fine- and coarse-grained $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *Phys Rev B* 73:094124
47. Thongbai P, Boonlakhorn J, Putasaeng B, Yamwong T, Maensiri S (2013) Extremely enhanced nonlinear current–voltage properties of Tb-doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *J Am Ceram Soc* 96:379–381
48. Thongbai P, Putasaeng B, Yamwong T, Maensiri S (2012) Modified giant dielectric properties of samarium doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *Mater Res Bull* 47:2257–2263
49. Xu D, Zhang K, Jiao L, He K, Xu HX, Zhao GP, Yu RH (2015) Microstructure and electrical properties of Sc_2O_3 -doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *Rare Met* 34:178–182
50. Lunkenheimer P, Krohns S, Riegg S, Ebbinghaus SG, Reller A, Loidl A (2009) Colossal dielectric constants in transition-metal oxides. *Eur Phys J Spec Top* 180:61–89
51. Wu J, Nan CW, Lin Y, Deng Y (2002) Giant dielectric permittivity observed in Li and Ti doped NiO. *Phys Rev Lett* 89:217601

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