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An aqueous-solution based low-temperature pathway to synthesize giant dielectric $CaCu_3Ti_4O_{12}$—Highly porous ceramic matrix and submicron sized powder

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A B S T R A C T

A simple, cost-effective and environment-friendly pathway for preparing highly porous matrix of giant dielectric material $CaCu_3Ti_4O_{12}$ (CCTO) through combustion of a completely aqueous precursor solution is presented. The pathway yields phase-pure and impurity-less CCTO ceramic at an ultra-low temperature (700 °C) and is better than traditional solid-state reaction schemes which fail to produce pure phase at as high temperature as 1000 °C (Li, Schwartz, Phys. Rev. B 75, 012104). The porous ceramic matrix on grinding produced CCTO powder having particle size in submicron order with an average size 300 nm. On sintering at 1050 °C for 5 h the powder shows high dielectric constants (>10^4 at all frequencies from 100 Hz to 100 kHz) and low loss (with 0.05 as the lowest value) which is suitable for device applications. The reaction pathway is expected to be extended to prepare other multifunctional complex perovskite materials.

1. Introduction

In the recent age of miniaturization of modern electronic devices, materials with high dielectric constant (ε') are indispensable [1]. Ba/Pb-based perovskite oxides, as, for example, $BaTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ are famous for their use as high-k capacitor materials with $\varepsilon' \sim 10{,}000$–$20{,}000$ and $\tan\delta \sim 0.01$–0.2, but they are not environment friendly for their toxicity. After the discovery of Pb-free piezoelectric ceramics [2] there is an increasing craze for Ba/Pb-free ceramic capacitor material. In relevancy it should be remembered that having a high dielectric constant is a necessary condition for one good ceramic material but is not sufficient alone, it should have a low dielectric loss ($\tan\delta = \varepsilon''/\varepsilon'$ where numerator and denominator represents imaginary and real parts of the complex dielectric constant respectively), which is related with the loss of stored electricity.

$CaCu_3Ti_4O_{12}$ (CCTO) is a non-ferroelectric material [3] having a very high dielectric constant (~10,000 for bulk and ~80,000 for single crystals at room temp.) [4] which remains more or less constant over a broad temperature range (from 100 K to 400 K below 1 MHz) [5] and also having a moderately low dielectric loss ($\tan\delta \sim 0.1$ at room temperature and at 1 MHz frequency) can serve the purpose very well and therefore has been at focus of intense research in the present decade with regard to both technological [6] and scientific aspects [7]. Generally ferroelectric materials with a non-centrosymmetric structure are most often used in high-dielectric applications and hence the observation of giant dielectric constant in CCTO is quite surprising since it is not ferroelectric [3] and shows a centrosymmetric cubic structure down to a temperature of 35 K. Several theoretical models and explanations are proposed [8–10] to understand the origin of this unusual property of CCTO among which the internal barrier layer capacitor (IBLC) model is most evidenced [11] and well-accepted one which attributes the unusual property to the existence of semiconducting grain and insulating grain boundary inside the ceramic.

A variety of methods [4,12–14] had been reported by several researchers to prepare this giant dielectric material. Among these the most adopted and traditional solid state reaction method lacks in terms of homogeneity of precursor materials due to often performed ball milling process which could not give efficient mixing. As a consequence the process requires higher sintering temperature and longer sintering time for solid state diffusion to occur for phase-formation. In the other hand solution based methods give molecular-level mixing in the precursor and thus produce phase in much less sintering time and at much lower sintering temperature. They are preferable for avoiding contaminations arising from milling media to the reacting raw materials since they

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does not need any ball-milling process as like solid state reaction pathway. Liu et al. have prepared CCTO from pyrolysis of an organic precursor solution with the help of glove-box facility and using 2-methoxy ethanol as a solvent [10] which is non-friendly to human body. Transition metal alkoxides (like Ti-isopropoxide) are highly reactive and undergoes rapid hydrolysis and polycondensation in the presence of even trace amount of water due to the high electropositive nature of the transition metal ion inside. Hence researchers use glove-box facility with controlled humidity (in the presence of dry argon or nitrogen gas) to avoid precipitation in order to prepare CCTO-precursor solutions [10]. In an alternative pathway to prevent alkoxide-hydrolysis large amount of organic stabilizers has to be added in organic solvent media which on combustion produces lot of carbon dusts and large extent of green house gas, CO_2. But these processes are relatively expensive, non-environment friendly and unconventional for large scale commercial production.

In this paper we are reporting a simple, cost-effective, relatively more environment-friendly (“Greener) aqueous-solution based pathway with addition of little amount of urea (for prohibition of production of hazardous nitrogen-oxides [15]) to prepare micro-porous CCTO matrix and submicron sized CCTO powder at as low temperature as 700 °C. The combustion residue obtained was seen to yield pure CCTO phase on calcinating at 700 °C with a highly porous microstructure (having pores typically of size 0.1–1.5). The highly porous microstructure might get importance due to structural lightweight, air inclusion leading to reduction of effective acoustic impedance, better machinability, impact resistance, etc. The porous CCTO ceramic matrix on grinding produced CCTO powder having particle sizes in submicron order. Prepared CCTO pallets on sintering showed high dielectric constant ($>10^4$ at all frequencies from 100 Hz to 100 kHz) and low loss (with 0.05 as the lowest value) on sintering at 1050 °C for 5 h and is therefore suitable for device applications. The same methodology can be applied to synthesize complex perovskite structure based materials.

2. Experimental

2.1. Materials

Calcium nitrate [$Ca(NO_3)_2$], copper nitrate [$Cu(NO_3)_2$] {both of analytical grade and from S-D Fine Chemical Limited}, Ti-isopropoxide [$Ti\text{-}(O^iPr)_4$, ^iPr = isopropyl group] {>99%, from Sigma–Aldrich} were purchased and used as metal-ion sources without further purification. nitric Acid (AR grade from S-D Fine Chemical Limited) was used as an oxidizing agent and double distilled water was used as a solvent and other purposes like washing throughout the experiment.

2.2. Synthesis of precursor solution and its thermolysis

To 50 ml of de-ionized water in a beaker, required amount of Ti-isopropoxide corresponding to 0.1 M CCTO precursor solution was added drop-wise with a gas-tight syringe in the presence of continuous stirring. Immediate formation of white polymeric gel of titanium hydroxide was noticed. The reaction system was cooled in an ice-bath for half an hour. Concentrated nitric acid (∼16 M solution in water) of required amount was added very slowly and drop-wise to the reaction mixture with continues stirring. Then it was kept in ice-bath for 1 h while stirring slowly. The white precipitate of polymeric hydroxide gel got dissolved as titanium oxynitrate. After then required amounts of calcium and copper nitrate, according to proper stoichiometric ratio of metallic ions were added to the solution and was stirred to dissolve while keeping the solution in ice-cool condition. Next the solution was heated inside a furnace first at 120 °C to boil-off water and then at 350 °C for decomposition of nitrates. A dark blue dry powder was obtained which was used for thermo-gravimetric analysis. This powder was calcinated at different temperatures (from 600 °C to 750 °C) for 2 h inside a muffle furnace to obtain pure-phase $CaCu_3Ti_4O_{12}$ powder.

For characterization of dielectric properties, circular pallets of uniform thickness were prepared from the calcinated powder. Required amount of 5% poly vinyl alcohol (PVA) solution was added as binder to the calcinated CCTO powder, mixed thoroughly, put inside a die and pressed with 15 kPa pressure with the help of a hydraulic-press, The resulting pallets were of 3 mm diameter and 1 mm thick. The pallets was heated at 350 °C for half an hour to remove PVA and then sintered at 1050 °C for 5 h inside a muffle furnace.

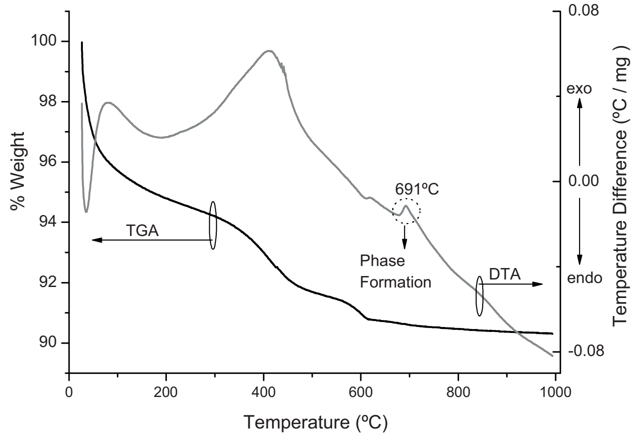

Fig. 1. TGA-DTA curves of as prepared powder from solution combustion.

2.3. Characterization of the as prepared and calcinated powder

The powder prepared in situ through combustion of precursor-solution and those obtained after calcinations at different temperatures were characterized with the help of X-ray diffraction (BRUKER D8 Advanced X-Ray Diffractometer). Simultaneously recorded thermogravimetry and differential thermal analysis (TGA–DTA) of the dark blue fluffy mass obtained from combustion of precursor solution was done with the help of a thermal analysis instrument (TA Instruments, DA800). Morphology of the samples was investigated with the help of a Field Emission Scanning Electron Microscopy (FESEM, TECHNEI Company). Energy dispersive X-ray analysis (EDAX) was also performed with the same instrument. For the sake of dielectric properties measurement silver paste was coated on both the sides of sintered pallets (in order to achieve metal–insulator–metal (M–I–M) configuration) and dielectric properties of the pallets were measured with the help of a Kethley precision LCZ meter (model no. 3330).

2.4. Probable reaction pathway

Addition of Ti-(isopropoxide) {$Ti(O^iPr)_4$, ^iPr = isopropyl group (C_3H_7-)} to water hydrolyses it and produces polymeric white gel of Ti-hydroxide {$Ti(OH)_4$}. Subsequent addition of concentrated nitric acid (HNO_3) in ice-cold condition produces water soluble titanium oxynitrate {$TiO(NO_3)_2$}. To avoid formation of nitrogen oxides addition of excess amount of HNO_3 should be avoided. Cooling is required in order to prevent the formation of titania (TiO_2) at this stage. On combustion with urea (H_2NCONH_2) titanium oxynitrate and other metal-nitrates decompose to pro-

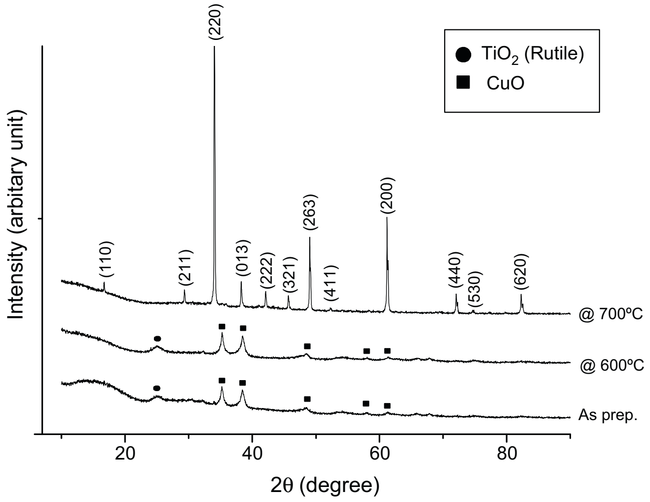

Fig. 2. X-ray diffraction pattern of powders as prepared from solution-combustion and calcinated at different temperatures. The top-most pattern is indexed according to JCPDS data (card no. 75-2188).

duce respective oxides [15]. Urea reduces nitrates to non-toxic and environment friendly native nitrogen which otherwise produces hazardous nitrogen-oxides [17]. The smaller amount of calcium oxide might be responsible for its absence in the X-ray diffractogram of as prepared mass. At higher temperatures during sintering the oxides react together to produce polycrystalline powder of $CaCu_3Ti_4O_{12}$. The effective molecular level mixing of the oxides generated from solution combustion probably reduces the diffusion path required for phase formation thus yielding the phase at much lower temperature compared to ball-milled ones.

$$Ti(O^iPr)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4^iPrOH[^iPr- = C_3H_7-]$$

$$Ti(OH)_4 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 3H_2O$$

$$2TiO(NO_3)_2 + 4CO(NH_2)_2 + O_2 \rightarrow 2TiO_2 + 6N_2 + 4CO_2 + 8H_2O$$

$$2M(NO_3)_2 + 4CO(NH_2)_2 + O_2 \rightarrow 2MO + 8N_2 + 4CO_2 + 8H_2O \quad [M = Ca, Cu]$$

$$CaO + 3CuO + 4TiO_2 \rightarrow CaCu_3Ti_4O_{12}$$

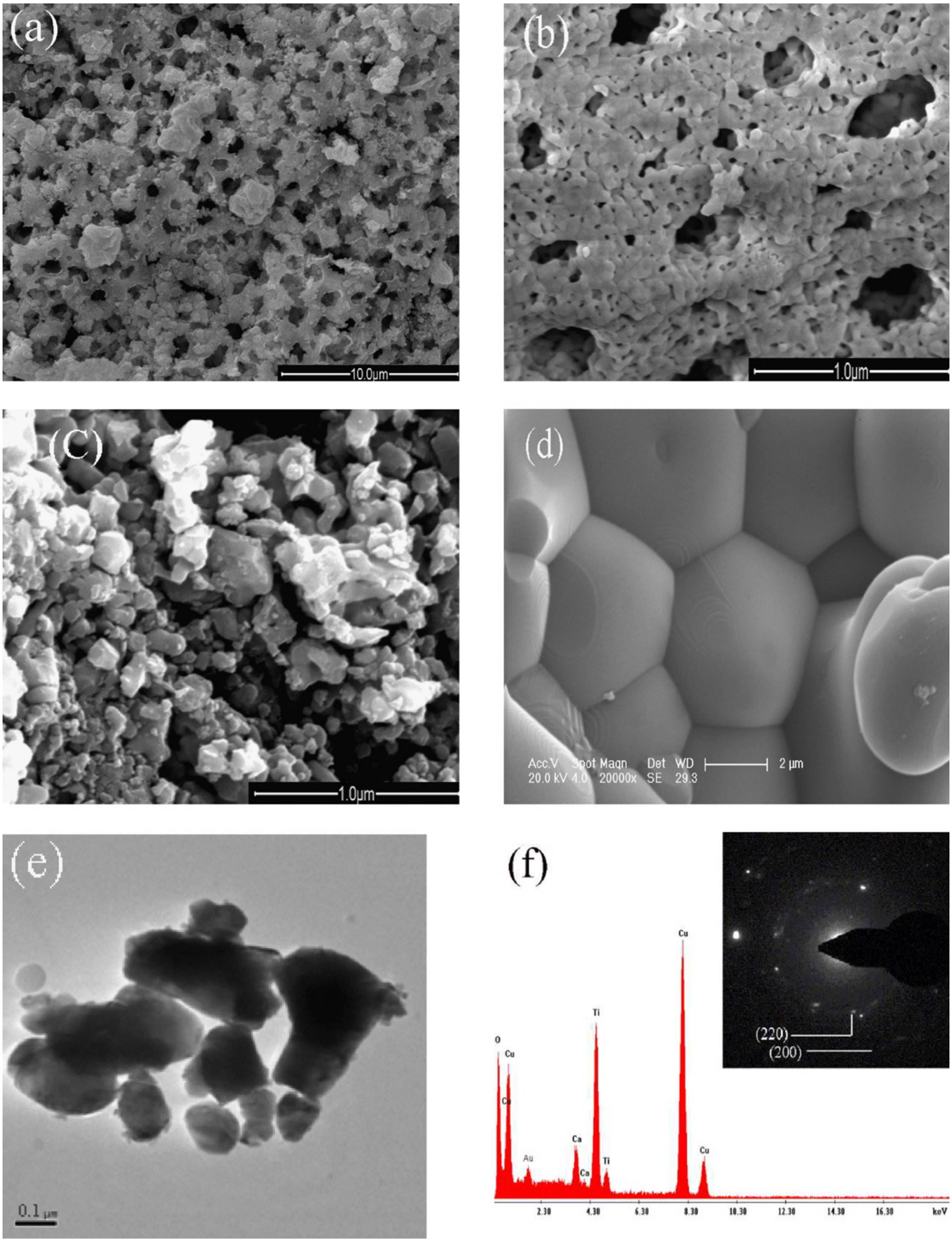

Fig. 3. (a)–(d): Scanning electron micrographs of 700 °C sintered solution combustion residue, (a) low magnification, (b) high magnification, (c) powder obtained on hand-grinding calcinated at 700 °C and (d) powder sintered at 1050 °C. (e) Transmission electron micrograph of $CaCu_3Ti_4O_{12}$ powder calcinated at 700 °C. (f) Energy dispersive analysis of X-ray (EDAX) spectrum of powder calcinated at 700 °C, the inset in this picture shows SAED pattern obtained from TEM investigation.

3. Results and discussion

3.1. Thermal analysis of combustion residue

Thermal analysis experiment of as prepared fluffy mass obtained from combustion of precursor solution was done in the presence of dry air flow and with a heating rate of 5 °C. The resulting TGA-DTA diagram is given in Fig. 1. A total weight loss of around 9.5% occur on heating which might be attributed to the loss of carbon, produced from burning of isopropanol and absorbed water on thermal treatment. Initial ~4% weight loss up to 100 °C is probably due to loss of absorbed water. This appears as an endothermic peak on the DTA curve. During the formation of titanium oxynitrate from titanium-isopropoxide, isopropanol is generated. This carbonaceous compound produces carbon on pyrolysis. The continuous loss of weight in the TGA curve up to 600 °C may be attributed to the oxidative-removal of C as CO_2 due to heating in the presence of air-flow. This generates a big exothermic peak near 420 °C and terminates at 618 °C with a small change in weight. Then onwards there is hardly any weight change in the TGA curve implying no removal of any constituents. At 691 °C the DTA curve shows an exothermic peak whereas there is no change of sample-weight, as evident from TGA curve. This clearly indicates the occurrence of phase formation at 691 °C as there are no other peaks in the DTA curve.

3.2. X-ray diffraction analysis

The powders as-prepared from solution combustion and calcinated at different temperatures were subjected to X-ray diffraction and the resulting diffraction patterns are given in Fig. 2. From the X-ray diffractograms it is evident that the powder calcinated at 700 °C has the proper $CaCu_3Ti_4O_{12}$ phase. Powders as prepared from solution combustion and calcinated at lower temperatures show peaks characteristics of rutile TiO_2 and CuO. The XRD pattern for the powder calcinated at 700 °C shows its polycrystalline nature and absence of any impurity peak proves its high purity. The X-ray diffraction pattern of this powder was indexed according to JCPDS data (card no. 75-2188).

3.3. Morphology investigations

Field emissive scanning electron micrographs of residue obtained from combustion of precursor solution are shown in Fig. 3(a) and (b) at lower and higher magnifications respectively. It can be noticed from these micrographs that the combustion generated ceramic matrix it highly porous, having pores in the range of ~0.1–1.5 μm sizes. Fig. 3(c) and (d) shows the SEM images of CCTO powder obtained on grinding as prepared combustion residue calcinated at 700 °C and sintered at 1050 °C respectively. Fig. 3(e) shows the transmission electron micrograph of the sample calcinated at 700 °C. From Fig. 3(c) and (e) we can predict the average particle size of the $CaCu_3Ti_4O_{12}$ powder calcinated at 700 °C is ~300 nm. The corresponding EDAX spectrum is shown in Fig. 3(f) which shows no impurity elemental peak except gold which was sputtered during sample preparation to facilitate electronic conduction. Thus the synthesis method we followed produces submicron sized CCTO powder with high purity. The inset in Fig. 3(f) shows SAED pattern obtained from TEM investigation which can be indexed accordingly. The sintered sample shows clear single crystalline grains with an average grain size of 2–3 μm as revealed from Fig. 3(d). As a consequence of heat treatment grain size enhances during sintering. Therefore the size and morphology of the CCTO powder can be varied by varying the temperature of heat treatment.

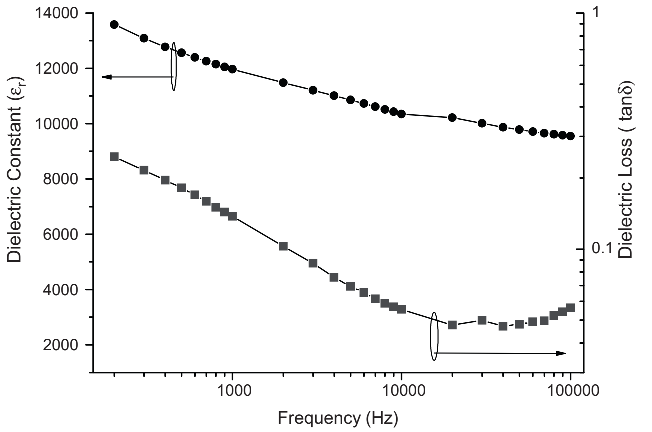

Fig. 4. Frequency dispersion of real part of dielectric constant (ε_r) and dielectric loss (tan δ) of CCTO pallet sintered at 1050 °C for 5 h.

3.4. Dielectric properties of sintered pallets

Dielectric properties of pallet sintered at 1050 °C for 5 h were measured in metal–insulator–metal (M–I–M, where Ag acts as metal and CCTO insulator) configuration and the resulting frequency dispersion of dielectric constant (ε_r) and dielectric loss (tan δ) is given in Fig. 4. From the dispersion it is evident that the dielectric constant of the sintered pallet is more than 10,000 at all frequencies and dielectric loss is as low as 0.05. The nature of change of dielectric constant with frequency is quite flat although it decreased monotonically whereas the dielectric loss value initially reduced, passed through minima and then increased with frequency variation. This kind of behavior of tan δ with frequency is in agreement with the model proposed by Goswami and Goswami [16]. Therefore pallets of $CaCu_3Ti_4O_{12}$ prepared through the associated method have a fairly high dielectric constant and considerably low dielectric loss which is suitable for many device applications.

4. Conclusion

In summary giant dielectric material $CaCu_3Ti_4O_{12}$ had been prepared through a simple, cost-effective, environment friendly and energetically beneficent pathway involving solution-combustion of an aqueous precursor solution. The metal-ion precursors are mainly inorganic salts of corresponding metals except Ti-isopropoxide which was hydrolyzed and converted in situ to water soluble Ti-oxynitrate by application of nitric acid. On combustion with urea as the external fuel the precursor solution generated precursor fluffy mass which on calcination produced pure CCTO phase at as low temperature as 700 °C. The product was investigated with the help of XRD and EDS for confirmation of phase-purity and elemental composition. On microscopic investigation the matrix was seem to be nano-crystalline and highly porous with pore sizes in the range of ~0.1–1.5 μm. Simple hand-grinding of the calcinated porous ceramic matrix yielded submicron-sized CCTO powder with average crystallite size of 0.3 μm as revealed by SEM and TEM studies. On sintering at 1050 °C for 5 h the powder shows a high dielectric constant (>10^4 at all frequencies from 100 Hz to 100 kHz) and low loss (with 0.05 as the lowest value) which is comparable to CCTO prepared by other methods and also suitable for device applications. We expect our pathway to be extended to other multifunctional perovskite oxides as well.

References

[1] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Oxford University Press, London, 2000.

[2] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Nature (Lond.) 84 (2004) 432.

[3] D. Fu, H. Taniguchi, T. Taniyama, M. Itoh, S.-y. Koshihara, Chem. Mater. 20 (5) (2008) 1694–1698.

[4] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, Solid State Chem. 323 (2000) 151.

[5] A.P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, S.M. Shapiro, Solid State Commun. 217 (2000) 115.

[6] W. Si, E.M. Cruz, P.D. Johnson, P.W. Barnes, P. Woodward, A.P. Ramirez, Appl. Phys. Lett. 81 (2002) 2056.

[7] L. He, J.B. Neaton, M.H. Cohen, D. Vanderbilt, C.C. Homes, Phys. Rev. B 65 (2002) 214112.

[8] D.C. Sinclair, T.B. Adams, F.D. Morrison, A.R. West, Appl. Phys. Lett. 80 (2002) 2153–2155.

[9] P. Lunkenheimer, V. Bobnar, A.V. Pronin, A.I. Ritus, A.A. Volkov, A. Loidl, Phys. Rev. B 66 (2002) 52105.

[10] J. Liu, C. Duan, W.N. Mei, R.W. Smith, J.R. Hardy, J. Appl. Phys. 98 (2005) 093703.

[11] T.-T. Fang, C.P. Liu, Chem. Mater. 17 (2005) 5167–5171.

[12] P. Jha, P. Arora, A.K. Ganguli, Mater. Lett. 57 (2003) 2443–2446.

[13] S. Jin, H. Xia, Y. Zhang, J. Guo, J. Xu, Mater. Lett. 61 (2007) 1404–1407.

[14] J. Liu, Y. Sui, C.-g. Duan, W.-N. Mei, R.W. Smith, J.R. Hardy, Chem. Mater. 18 (2006) 3878–3882.

[15] R.K. Lenka, T. Mahata, P.K. Sinha, A.K. Tyagi, J. Alloys Compd. 466 (2008) 326–329.

[16] A. Goswami, A.P. Goswami, Thin Solid Films 16 (1973) 175.

[17] Y. Shanmugam, F.-Y. Lin, T.-H. Chang, C.-T. Yeh, J. Phys. Chem. B 107 (2003) 1044–1047.