An Overview on Recent Developments in the Synthesis, Characterization and Properties of High Dielectric Constant Calcium Copper Titanate Nano-Particles

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Received: December 15, 2013; Accepted: May 05, 2014; Published: May 05, 2014

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Abstract

The potential demand for miniaturization of electrical and electronic devices has raised a serious challenge for the development of capacitors with high dielectric constant and low loss. The high dielectric constant calcium copper titanate, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), and its isomorphs have attracted much attention for the development of promising capacitor materials for electronic industries. Improving the synthetic technology and dielectric properties of these materials is a current focus of research and development in the area of materials chemistry. Because of their improved properties due to size and structure, the nanometer-sized particles (with dimensions smaller than 100 nm) have attracted considerable interest for a wide variety of applications, including electronics, ceramics and as catalysts. The wet chemical methods provide atomic level mixing of individual components and result in the formation of nano-crystalline materials at much lower temperature compared to solid state reactions. Many chemical methods, such as, sol-gel, co-precipitation, precursor solution technique, hydrothermal process, carbo-thermal reduction, microwave heating, spray pyrolysis, co-precipitation and micro-emulsion drying are already reported for the synthesis of CCTO ceramics. The present communication gives a current overview of the synthetic procedures used for the production of CCTO and doped derivatives. In addition to already established conventional routes of preparation, alternative procedures are also outlined.

Keywords: Calcium copper titanate; Synthesis of CCTO; Nano-crystalline; Sol-gel processing; Semi-wet route; Dielectric properties

Introduction

In the modern age of science there is continuous demand for miniaturization of electronic devices (cell phones, digital cameras, note book, computers, TV etc.) and there is continuous interest to develop capacitor materials with high dielectric constant and low loss for application to microelectronics, microwave, memory and capacitance based energy storage devices [9]. Electro-ceramic materials are considered essentials due to their excellent dielectric, piezoelectric and electromechanical properties, which are used in defense, aerospace and civil sectors such as aerospace, transducers and sensors and gyroscopes. The power capacitors

are the passive critical components in aircraft instrumentation, missile systems, satellite positioning equipment, ignition systems, etc. to provide a static source of power in electrical distribution systems. Electrical energy storage plays a key role in mobile electronic devices, stationary power systems, hybrid electric vehicles and pulse power applications. In particular, there is a growing need for capacitors that can accumulate a large amount of energy and then deliver it nearly instantaneously. This kind of “pulse power” is needed for a variety of military and commercial applications. Dielectric materials can be used to store electrical energy in the form of charge separation when the electron distributions around constituent atoms or molecules are polarized by an external electric field. Requirement of an ideal capacitor material is that it should have (1) high dielectric constant (10^4 - 10^6) (2) low dielectric loss ($\tan \delta = 0.01$ - 0.0001) (3) high thermal stability (stable up to 500°C) and (4) no variation in dielectric constant with temperature and frequency of current in any region. Calcium copper titanate is a member of an oxide family whose general formula is $\text{ACu}_3\text{Ti}_4\text{O}_{12}$. Depending on different values of A one can get different isomorphs of this family. When A is calcium, the corresponding compound will be $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and this compound was discovered by Deschanvres et al. [1]. This family was expanded and its accurate crystal structures were determined by Bochu et al. [2]. According to them this compound belongs to BCC system with $\text{Im}\bar{3}$ space group and $7.391\text{\AA}$ unit cell length, and there are two formula units per unit cell of the compound. While two calcium atoms sit at the corners and body center of the cube and six copper atoms are located at its six face centers and twelve edge centers, the eight Ti atoms are present at the centers of the octahedron facing each other with bridging copper atoms bonded to oxygen. Recently, high resolution X-ray diffraction patterns and neutron diffraction studies by Adams et al. [3] in 2006 have shown that these compounds crystallize as perovskite structures where TiO_6 octahedra are tilted to produce square-planer environment for each copper ion. This tilting alters the coordination environments of A-site cations, leading to a 4-coordinate square-planar environment for Cu and

12-coordinate icosahedral environment for Ca. It is the mismatch in size and bonding preferences of these two ions and titanium that drive the large octahedral tilting distortion. $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ type oxides with complex perovskite structure show high dielectric constant leading to many important applications. Presently we use BaTiO_3 or relaxor ferroelectrics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [PMN], $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [PZN], and $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ [PLZT], which are not environmentally friendly as capacitor materials (dielectric constant ≈ 1000 -20,000) [4]. Problems with BaTiO_3 are that it is a ferroelectric perovskite which is quite unstable and shows phase transitions. Its dielectric constant being highly unstable with temperature (T), it is not suitable for use at an elevated temperature. For this reason, a thermally stable high dielectric constant calcium copper titanate, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), which belongs to $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ family, first reported by Subramanian et al. [5] in the year 2000 is the best choice. The very high dielectric constant ($\sim 10^4$) exhibited by (CCTO), which is nearly constant in the temperature range, 100K to 600K, makes it a promising material which can lead, to many important applications in microelectronics and memory devices as static dielectric constant of a material ultimately decides the degree of miniaturization. It may be widely used in the electronic industries to manufacture electronic components such as multilayer capacitor (MLCC), DRAMs (Dynamic Random Access Memory), microwave devices, electronic devices in automobiles and aircrafts. Despite the fact that much research work has been done to reveal nature and origin of the giant dielectric constant of CCTO ceramics, it still remains controversial and unsolved to date. At present, a possible explanation that an internal barrier layer capacitance (IBLC) model between the insulating grain boundaries and semiconducting grains, is widely accepted by the researchers. High dielectric constant values may be variously attributed to [6-8]:

1. The barrier layer capacitance arising at twin boundaries
2. Disparity in electrical properties between grain interiors and Grain boundaries
3. Space charge at interfaces between the sample and the electrode contacts
4. Polarizability contributions from lattice distortions
5. Differences in electrical properties due to internal domains
6. Dipolar contributions from oxygen vacancies
7. The role of Cu off-stoichiometry in modifying the polarization mechanisms
8. Cation disorder induced planer defects and associated in homogeneity.

A variety of methods [10-13] has 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. In addition, the process requires higher sintering temperature and longer sintering time for solid state diffusion to occur for single

phase-formation. Therefore, the chemical methods resulting in good homogeneity in CCTO and their isomorphs at lower sintering temperature in shorter sintering time is the current approach for the synthesis of the best quality materials. With a view to obtain high dielectric constant and low loss CCTO, effect of substitution on it has been studied by various workers [14-17] and they report wide variation in these values as a result of this exchange. Fang and Shiao [18] have studied the effect of sintering time from zero time to 20 hrs at 1035 °C on the dielectric properties of CCTO and have found that it varies from 1000 to 18000 in this time duration. Driven by the needs, and the peculiar properties of nano-particles due to their small size and large surface area, various aspects of Ca-Zn exchange have been studied. For this CCTO and their isomorphs with zinc have been prepared by semi-wet route involving different sintering time. In addition, the effects of synthetic methods have also been studied. They were characterized by X-ray and TEM techniques and their dielectric properties were studied in the different temperature and frequency regions. Although a large number of papers [19-23] have been published by authors on CCTO where cationic exchange reactions have been studied, in the present paper an overview of the summary of synthesis, characterization by X-rays and dielectric properties for systems giving nano-particles have been reported. In the absence of any review on the CCTO, in general, and CCTO nano-particles in particular, the present paper gives an account of recent development and latest information on calcium copper titanate which will be quite useful for the new workers in this area.

Synthetic Routes of CCTO

With a view to obtain high dielectric constant and low tangent loss calcium copper titanate, Ca, Cu, and Ti exchange was studied. CCTO and its substituted isomorphs have been synthesized by different methods, namely, (i) solid-state route (ii) chemical route (iii) combustion route and (iv) semi-wet route. These resultant products were characterized by X-ray and transmission electron microscopy (TEM) techniques. The dielectric constant and the corresponding dielectric loss of these electro-ceramics have been studied in the temperature range 100K to 600K at various frequencies. Assessment of the influence of the different processing parameters, such as, sintering time and sintering temperature on the dielectric properties were also studied.

Dry method

The perovskite oxides are generally synthesized by conventional solid-state route [13] or dry method. In this route, oxides of various cations with suitable liquid (acetone or ethanol) are mixed in stoichiometric ratio and ground to fine powder using a pestle-mortar. Dried mixed powder is calcined at a particular temperature for a certain period of time. The calcined powder is ground again and converted in to fine powder. An optimum amount of a suitable binder, polyvinyl alcohol (PVA) is added to the powder and mixed uniformly and then it is pressed in to a suitable shape. The resulting product is first heated slowly to a particular temperature to remove the binder and then the temperature of the sample is increased to a particular value and maintained at this value for certain duration for annealing. After

annealing, the sample is cooled under controlled rate of cooling. The final resulting product is achieved by diffusion of metal ions at high temperature. Asystematic flow chart is shown in Figure 1.

Wet methods

The dry method used for the synthesis of CCTO requires relatively long reaction time and high temperature condition. In addition, some other secondary phases also appear during the synthesis because of limited atomic diffusion through micrometer sized grains. Therefore, repeated grinding, mixing and annealing is required at high temperature to attain chemical homogeneity.

However, this does not lead to chemical homogeneity at micro level in the end product. On the other hand, the wet chemical methods [24-26] provide atomic level mixing of individual components and result in the formation of nano-crystalline materials at much lower temperature compared to solid state reactions. There are many chemical methods, such as, sol-gel, co-precipitation, precursor solution technique and hydrothermal process which have been used for the synthesis of ceramics. A systematic flow chart for "wet method" is shown in Figure 2.

Pechini's method: Pechini's method [27] was developed by M.P. Pechini for the synthesis of titanates and niobates for the capacitor industry. The modified Pechini method referred as the citrate gel process or the amorphous citrate gel process has been used for the preparation of a wide variety of ceramic oxide powders. This technique involves mixing of solutions of a metal precursor and an organic poly-functional acid possessing at least one hydroxyl group and one carboxylic acid group such

Figure 1: Flow chart for the synthesis of materials by solid state route.

Figure 2: Flow chart for the synthesis of materials by wet method.

as citric acid, glycine, tartaric acid and glycerol, which results in complexation of the metal by the poly-carboxylic acid. The solutions are heated to evaporate water and after its complete removal the highly viscous resin is formed. The resin is then heated to decompose the organic constituents, ground and finally calcined to produce the powder. Pechini route achieves very good chemical homogeneity due to mixing of metal cations on the atomic scale during the polymerization process and this is maintained in the formation of the resin. If none of the constituents volatilizes during the calcination step, the cation composition remains identical to that of the original solution. The disadvantage of the above method is that the material formed from the decomposition of resin is not in the form of a fine powder but consists of charred lumps. These lumps have to be ground and then calcined to produce the final powder. Care should be taken to see that the grinding step may not introduce impurities into the powder. As such the resulting calcination step produces hard agglomerates.

Glycine gel method: Glycine gel nitrate process is one of the types of combustion methods for the synthesis of ceramic powders. A highly viscous mass formed by evaporation of a solution of metal nitrates and glycine is ignited to produce the powder [28]. Glycine is a complexing agent and prevents the precipitation of the metal ions as the water is evaporated. It can form complex with cations at both the carboxylic end and the amino group end as illustrated in Figure 3.

Glycine also serves another important function by providing a fuel for the ignition step of the process as it is oxidized by the nitrate ions. The reactions occurring during ignition are highly explosive and extreme care is required during this step. Normally, only small quantities should be ignited at a time. Under

Figure 3: Zwitter-ionic glycine molecule complexing Mn^{n+} .

well controlled conditions, a loose mass of very fine crystalline powder is obtained after ignition, so, in contrast to the Pechini method, no grinding is required. The very fine size and crystalline nature of the powder are believed to be direct result of short exposure to high temperature during the ignition step. Glycine gel nitrate process, therefore, offers a relatively/inexpensive route for the synthesis of very fine chemically homogeneous powder. It has been used for the synthesis of simple oxides as well as complex oxides e.g. manganite, chromites, ferrites and oxide superconductors.

Semi wet method: This route is modified sol-gel technique [29]. It is also named as citrate-nitrate gel chemical method which is a type of combustion synthesis technique. Combustion synthesis is generally used to obtain multi-component single phase material. The combustion technique is based on redox reaction between a fuel and oxidant present in the precursor solution. Generally, citric acid, urea, ethylene glycol etc. are used as a fuel and, nitrates of different metals are used as an oxidant. The chelating agents like EDTA, acetic acid etc. can form complex with metal ions present in the precursor solution and act as fuel. This complex, on dehydration, produces a viscous gel which on further heating self-ignites with the evolution of huge amount of gases. This leads to the development of porous floppy ash. Fine phase pure powder can be obtained on further calcinations of the ash at high temperature. In semi-wet route, TiO_2 suspension was developed in our laboratory with citric acid solution. All the metal cations were taken as nitrate except TiO_2 which was taken as solid. Citric acid was used as the fuel. Flow chart for the synthesis of CCTO and its isomorphs is given in Fig. 4 and a probable complex of metal cations and the citric acid is shown in Fig.5. In this route, standard solutions of nitrate of each metal ion were prepared using distilled water. Solutions of metal nitrates in stoichiometric amounts were mixed in a beaker. Stoichiometric amounts of solid TiO_2 and aqueous solution of citric acid (equivalent to metal ions) were added to the solution. The solution was then heated on a hot plate with magnetic stirrer at 70-80°C to evaporate water. Dehydration of the homogeneously mixed solution during heating caused the development of a gel. This gel on further heating self-

ignites followed by its swelling. This ignition product as ash was voluminous and floppy in nature.

Synthesis of CCTO Nano-particles-The Current Status

Dry methods

Solid state synthesis is a technique used to produce materials by the reactions carried out at high temperature and pressure. This method is generally used for the mass production of unique, advanced structures for dielectric and piezoelectric. It is a conventional method for preparing ceramics and includes several successive steps of intimate grinding and annealing of the stoichiometric mixture of starting materials.

Solid-state reaction: The solid state synthesis of CCTO powders typically starts with the mixing of precursors by ball milling or other techniques. The most commonly used precursors are $CaCO_3$ (99.9%), CuO (99.9%) and TiO_2 (99.9%) of high purity chemicals. However, other precursors can also be used in the form of acetate. Generally, the solid state method cannot produce CCTO powders in nanometer scale. However, by modifying this method and parameters it provides the CCTO powders with an average particle diameter of around 500 nm.

Wang et al. [30] synthesized CCTO using nano-size powders containing particle size: 30 nm ($CaCO_3$, 99.9%), 25~55 nm (CuO , 99.95%) and 30 nm (TiO_2 , 99.9%) and found particle size in the range 0.1~0.3 μm . The samples synthesized with nano-size powders have homogenous microstructure. SEM observation reveals that the particle size of powders calcined with nano powder and micro powder is about 0.5 ~ 1.0 μm (a) and 1 ~ 2 μm (b), respectively. The microstructure of nano-sized derived sample is densified with fine and homogeneous grain distribution, and relative density is 94%, which is higher than that of 91% derived from micro-meter powder. The CCTO obtained using nano-size raw materials show its dielectric constant by an order more than that produced from submicron particles.

Wet methods

Wet chemical synthesis routes, such as sol-gel, hydrothermal/solvothermal, or co-precipitation methods, have more advantages over solid-state reactions in achieving better homogeneity and mixing of the starting compounds on molecular level.

Sol-gel processing: Sol-gel processing is a technique which produces the high purity and homogeneity and lower processing temperatures ceramic powders than traditional ceramic powder methods. Sol-gel processing enables the control of the structure of a material on a nanometer scale from the earliest stages of processing due to mixing in atomic scale. Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters in the range of 1-100 nm. A gel is an interconnected, rigid network with pores of sub-micrometer dimensions and polymeric chains whose average length is greater than a micrometer. The different precursors, sintering temperature, particle size and dielectric properties have been given in table 1.

Masingboon et al. [31] fabricated the nano-crystalline $CaCu_3Ti_4O_{12}$ powders with particle sizes of 50-90 nm by a simple

method using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, titanium(di-isopropoxide) bis(2,4-pentanedionate) and freshly extracted egg white (ovalbumin) in aqueous medium. The average size of the calcined CCTO powders at 700°C and 800°C were found to be 60 nm and 100 nm, respectively. Some agglomerates were observed in all of the calcined powders. The observed nano-crystalline nature of CCTO by TEM analysis of calcined powder is shown in Figure 6. The electron diffraction of particles (84.9 ± 15.3 nm) with higher calcination temperature (800°C) contains more intense spots (as shown in the Figure 6) than that at 700°C (56.7 ± 7.9 nm) indicating thereby that the former has size larger than the later.

Thomas et al. [32] developed a wet chemical method for the preparation of complex oxalate precursor, $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$ (CCT-OX), and the precipitate that obtained was confirmed to be monophasic by the wet chemical analyses, X-ray diffraction, FTIR absorption and TG/DTA analyses. The thermal decomposition of this oxalate precursor led to the formation of phase-pure calcium copper titanate, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) at 680°C. The precursor gives rise to phase-pure nano-particles of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) powders with a crystallite size varying from 30–80 nm when heat treated at >680°C; the bright-field TEM micrographs shown in Figure 7 revealed that the sizes of the as synthesized crystallites are in the nanometer range. The ceramic powders so obtained had excellent sinter ability resulting in high density ceramics which exhibited giant dielectric constants up to 40000 (1 kHz) at 25°C, accompanied by low dielectric losses, <0.07.

Sen et al. [33] developed a novel, low temperature synthetic technique for fabrication of nano-crystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic powders by a metal ion–ligand complex based precursor solution

Figure 4: Flow chart for the synthesis of materials by semi-wet route.

Figure 5: A Probable structure of metal-citrate complex.

evaporation method using inexpensive and easily available reagents with high purity raw materials, calcium carbonate (CaCO_3), copper(II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), ethylenediaminetetraacetic acid (EDTA), tri-ethanolamine (TEA) and titanium tartrate. XRD analysis confirmed the formation of cubic phase, with a lattice parameter value of $7.3985 \text{ \AA}$. Spherical particles of average 65 nm size were observed from TEM micrographs after calcination at 700°C which was in good agreement with the particle size obtained from the Reitveld analysis.

Banerjee et al. [34] has developed a capillary-enforced template-based method applied to fabricate calcium copper titanate nano-tubes (diameter ~200 nm) by filling sol-gel CCTO precursor solution into the nano-channels of porous anodic aluminum oxide (AAO) templates and subsequent heating for phase formation and removal of nano-channel templates by applying basic solution. They suggested that this facile method of preparing the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano-tubes at a large scale might be important for many applications in nano-devices. XRD and selected-area electron diffraction (SAED) investigations demonstrated that post annealed (750°C for 1 h) CCTO nanotubes were polycrystalline with a cubic pseudo-perovskite crystal structure. The FE-SEM and TEM results showed that CCTO nanotubes were of uniform diameter (~200 nm) throughout their length.

Figure 8 shows TEM image of a CCTO nano-tube after complete removal of AAO template by dissolution in 6 M NaOH solution. It is clearly seen that nano tube is in hollow structure and enhanced scattering at edges of the tube makes it darker than the middle portion. The diameter of the nano-tube is almost uniform throughout its length which is approximately equal (slightly smaller) to channel diameter of the applied template. Figure 8(b) showed a typical HRTEM image of the wall of a CCTO nano-tube prepared with the help of AAO templates and revealed that the nano-tube is made up of a number of CCTO well-resolved nano-particles that are randomly oriented in the wall. High resolution TEM (HRTEM) analysis confirmed that the obtained CCTO nanotubes are made of randomly aligned nano-particles, 5-10 nm in size.

Amaral et al. [35] have reported the synthesis and characterization of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) powders prepared by two different wet-chemical methods: ethylene diaminetetraacetic acid-gel method (EDTA) and modified Pechini (MP) process and observed that in both cases, almost single-phase CCTO

Table 1: Precursors used in the sol-gel synthesis method, metal dopant, particle size, dielectric constant and dielectric loss of the resultant CCTO powders.

Ca Precursor	Cu Precursor	Ti Precursor	Dopant temperature	Metal Calcination	Particle size(nm)	tanδ	Ref
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	titanium(diisopropoxide)	700°C	60	5×10^4	0.2	[31]
CaCO_3	CuCl_2	TiOCl_2	680°C	30–80	4×10^4	0.07	[32]
CaCO_3	$[\text{Cu}(\text{CH}_3\text{COO})_2]$	titanium tartarate	700°C	65	-	-	[33]
$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	$[\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4]$	750°C	200	-	-	[34]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ti}(\text{OC}_4\text{H}_9)_4$	700 °C	50-100	1×10^4	-	[35]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Ti	800°C	60-80	1.06×10^5	-	[36]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	titanium isopropyl orthotitanate	700°C	50-150	5×10^3	0.37	[37]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ti}(\text{OC}_3\text{H}_7)_4$	800°C	90-120	5×10^4	6	[38]
$\text{Ca}(\text{Ac})_2 \cdot \text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	tetrabutyltitanate	750°C	30-80	-	-	[39]
$\text{Ca}(\text{C}_2\text{H}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Ti	800°C	80-200	9516	0.02	[40]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$[\text{Ti}(\text{OC}_3\text{H}_7)_4]\text{Co}$	800°C	70-80	2.5×10^4	-	[41]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ti}(\text{OC}_4\text{H}_9)_4$	800°C	100	5.9×10^4	0.06	[42]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$[\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4]$	800°C	200	-	-	[43]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ti}(\text{OC}_3\text{H}_7)_4\text{Zr}$	800°C	47-80	1.27×10^4	6	[44]
$[\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ti}(\text{OC}_4\text{H}_9)_4\text{Zn}$	1050°C	2 μm	2.2×10^4	0.098	[45]
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	titanium(dilsopropoxide)	700°C	300	$>10^4$	0.05	[46]
$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ti}(\text{OC}_4\text{H}_9)_4\text{Nd}$	800°C	120-250	1.12×10^4	0.12	[47]

Figure 6: Bright field TEM images with corresponding selected area electron diffraction (SAED) pattern of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders calcined in air for 8 h at different temperatures: (a) 700°C and (b) 800°C [31].

Figure 7: Bright field TEM image of CCTO with particle dimensions ranging from 30–80 nm [32].

Figure 8: TEM image of (a) CCTO nano-tube after complete removal of AAO template; (b) Single nano-tube surface revealing that it is comprised of a number of randomly oriented particles [34].

fine powders were obtained from the calcination of the gel precursors at lower temperatures and shorter times than those reported for the conventional solid state reaction process. The SEM image of the powder calcined at 700 °C and prepared by the MP method present nano-size particles in spherical form with size ranging between 50 and 100 nm. The grain size of sintered pellets produced from the powders obtained by the MP process present larger mean grain size compared to the pellets obtained from EDTA-gel method. This fact agrees well with IBLC model, and a higher dielectric permittivity was predicted for the samples produced by MP process than that by the EDTA method.

C. Kumar et al. [36] prepared the calcium copper titanate (CCTO) nano-powder by the sol-gel self-combustion method. The X-ray diffraction analysis indicated that the samples calcined at 800°C were fully crystallized in the CCTO phase. The atomic force microscopic studies showed that their particle size was in the range of 60–80 nm as given in Figure 9.

The absorption bands corresponding to vibrations of Cu–O, Ti–O–Ti and m Ca–O were observed at 512, 450 and 562 cm⁻¹ using FTIR. The CCTO pellets were sintered at low temperature of 950 °C. A large value of dielectric constant, in the order of 10⁶, was due to the low sintering temperature and uniform microstructure.

Kumar et al. [37] synthesized the nano-particles of CaCu₃Ti₄O₁₂ by sol-gel reaction route sintered at 1025°C with reduced sintering time and obtained CCTO samples with high dielectric constant $\epsilon \sim 5000$ and $\tan \delta \sim 0.37$ at 10 Hz. The TEM images of the as calcined powder at 700°C show large agglomerates of nano-particles in Figure 10. The average particle size was in the 50–150 nm range. The agglomeration may be due to strong inter-particle forces between the particles.

Jesurani et al. [38] prepared the precursor of CaCu₃Ti₄O₁₂ (CCTO) nano-particles by sol-gel method at 90°C. The dried precursor powder was milled and then calcined at 450°C, 550°C, 650°C, 800°C, 850°C and 950°C for 3 h. The single

Figure 9: AFM image of CCTO Nano-powder calcined at 800°C [36].

Figure 10: AFM image of CCTO Nano-powder calcined at 800°C [36].

phase formation of CCTO was analyzed by step by step using FTIR and XRD. The absorption bands corresponding to vibrations of Ca-O, Cu-O and Ti-O-Ti were observed at 606, 525 and 463 cm^{-1} using FTIR. The particle size from AFM is about 90–120 nm. The grain size varies from 500 nm to 6 μm as measured by FE-SEM. The FE-SEM micrographs clearly show bi-modal distribution of grains; the smaller grains have size range from 500 nm to 2 μm and the larger grains have size range from 2 to 6 μm . The bimodal distributions of grains indicate that the sol-gel derived CCTO powders have hard agglomerates which on sintering form large grains. The CCTO pellets were sintered at low temperature of 1040°C. A giant value of dielectric constant, of the order of 10^5 , was measured due to the low sintering temperature and dense microstructure.

Tian et al. [39] prepared $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano-powders by a sol-gel route with calcinations temperature 750°C, using tetra-butyl-titanate, calcium acetate and cupric nitrate as precursors. The xero-gel and the formation of single-phase CCTO with different calcining temperatures at 350°C, 550°C, and 750°C in air were confirmed by the FTIR analysis. When precursor powder was treated at 750°C for 3 h, the obtained sample shows pure CCTO XRD peaks indicating its high crystallization and good purity and the average size of the crystalline particles were calculated to be 50.3 nm based on the Debye-Scherrer formula. TEM image of the CCTO at 750°C showed that the size of nano-crystals is in the range 30–80 nm, which is roughly close to the size obtained from the “Debye-Scherrer” formula. The obtained $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano-powders were investigated as a gas sensitive material responding to ethanol atmosphere, and it showed high sensitivity for ethanol gas. Their studies, not only enrich the contents of CCTO chemistry, but are also beneficial to investigate their potential application in gas sensors.

Vangchangyia et al. [40] prepared CCTO ceramics using Ca- and Cu-acetates as starting raw materials by a modified sol-gel method with different calcining conditions and showed excellent dielectric properties. The precursor was ground and calcined in air at 850°C for 2 h (CCTO-1), 850°C for 8 h (CCTO-2), and 900°C for 4 h (CCTO-3) and was finally sintered in air at 1100°C for 6h. The microstructure of CCTO ceramics are shown in Figure 11(a-d). The presence of impurity phases in calcined powder at 850°C for 2 h has a significant influence on the microstructure of sintered CCTO-1 ceramic. The microstructure of the CCTO-1 ceramic shows a large amount of pores; CCTO-2 and CCTO-3 ceramics are relatively dense. Figure 11 (d) shows a TEM image of CCTO-3 particles, revealing a large distribution of particle sizes ~80–200 nm. At 1 kHz and at room temperature, the best CCTO ceramic can exhibit a high dielectric constant (ϵ_r) of 9516 with a very low dielectric loss, $\tan\delta \sim 0.020$. The minimum value of $\tan\delta$ is 0.018 at 2.5 kHz with $\epsilon_r \sim 9433$.

Jesurani et al. [41] successfully prepared the $\text{CaCu}_3\text{Ti}_{(4-x)}\text{Co}_x\text{O}_{12}$ (CCTCO, $0 \leq x \leq 1.0$) ceramics by sol-gel method. XRD analysis indicated that the ceramics consisted of a single phase, without structural change in CCTO. HRSEM image in Figure 12 of $\text{CaCu}_3\text{Ti}_{(4-x)}\text{Co}_x\text{O}_{12}$ where $x = 0, 0.02, 0.1, 0.2, 0.5$ and 1.0, showed that some CCTCO grains are distinguishable in lower

Figure 11: SEM images (a) CCTO-1, (b) CCTO-2, (c) CCTO-3 ceramic samples, and (d) TEM image of CCTO-3 powder [40].

concentration and appear to be highly agglomerate in higher doping concentration and enhanced the grain growth.

The grains were found to be regular and polyhedral type in the lower concentration of Co dopant. The un-doped specimen consists of some huge grains, surrounded by small ones. The dielectric study showed that the dielectric constant reached a value as high as ($\epsilon_r = 25,400$ at 1,000 and $\epsilon_r = 111,000$ at 1,050 °C) at a cobalt-doping concentration of $x = 0.2$ at low frequency (50 Hz) whereas the ϵ_r values of the samples with $x = 0.00, 0.02, 0.1$ and 1.0 remain most unchanged with good frequency stability at higher frequency and they are much smaller than those of the CCTCO (where $x = 0.2$ and 0.5).

Zhao et al. [42] synthesized CCTO nano-size powders by sol-gel route using analytical grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were used as the starting materials. The thermal decomposition process, phase structures and morphology of synthesized powders were studied by IR, DSC-TG, XRD, TEM and FT-IR spectrum of CCTO. Dry precursors showed that a strong and broad absorption band in the region of 2800–3600 cm^{-1} , centered at 3447 cm^{-1} , originated from the O-H vibration of weak-bound water, butanol and C-H vibration of alkyl groups. The characteristic absorption peaks of NO_3^- appear near the wave number 1382 cm^{-1} . The absorption peaks of 1636 cm^{-1} , 1543 cm^{-1} and 1045 cm^{-1} are attributed to the asymmetrical stretching vibration and the symmetrical stretching vibration of $-\text{COO}^-$. The investigation of DSC/TG showed that the main weight-loss and decomposition of precursors occurred below 450°C and CCTO crystallite gradually appeared and became stronger when the calcination temperature was higher than 700°C. CCTO-based ceramics with excellent dielectric properties ($\epsilon_{25} = 5.9 \times 10^4$, $\tan\delta = 0.06$ at 1.0 kHz) were prepared by sintering at 1125°C, and proposed that a conduction mechanism was responsible for the origin of giant dielectric constant in CCTO system.

Banerjee et al. [43] reported the low-dimensional fabrication of technologically important patterned nano-dots of giant dielectric material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) on platinized silicon substrate

with defined size, shape and separation using soft electron beam lithographic technique. The fabrication procedure is typically constituted of two steps. In the first step nano-fabrication was prepared on substrate surface by e-beam lithographic process. Next the sol-gel precursor solution of the CCTO made up using inorganic metal nitrates and Ti-iso-propoxide were spun-coated onto it which subsequently followed by drying, lift-off and annealing to yield nano-fabricated dense ceramic material. Phase purity and crystallinity of post-annealed dots were confirmed by X-ray diffraction studies. Morphology of the dots was investigated with atomic force microscopy where it was found that they have an average diameter of 200 nm with average height of 50 nm. TEM and EDX analysis of an isolated CCTO nano-dot is presented in Figure 13.

The size of the nano-structure is found to match well to that obtained from SEM studies. Some over growth can also be seen in the image. Corresponding selected area electron diffraction (SAED) pattern is given in Figure 13(b) which reveals the polycrystalline nature and the rings in the SEAD pattern corresponds to (422), (400), (013), (220) and (200) crystal planes of cubic pseudo-perovskite phase of CCTO. The EDX spectrum in Figure 13(c) confirmed the characteristics of all elements present in CCTO ceramic.

Jesurani et al. [44] successfully prepared the giant dielectric constant Zr substituted $\text{CaCu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ (CCTZO) with $x = 0.00, 0.02, 0.10, 0.20$ and 0.50 mol% nano powder by sol-gel technique with lower processing temperature from the metal nitrate solutions, titanium isopropoxide and zirconium oxy chloride. XRD analysis confirmed the formation of a single phase material in the ceramics calcinated at 800°C for 3 h. The crystal structure did not change on doping with zirconium and it remained cubic in all compositions. AFM studies in Figure 14 showed that the particle size of the CCTZO powder ranged from 47 to 85 nm and shapes of the particles were polyhedral in nature.

FE-SEM micrographs of the $\text{CaCu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ceramics showed that the grain size was in the range of 250 nm to 5 μm for these samples. When Zr concentration increases, the size of the in-boundary particles were found to be change. Increasing zirconium concentration on CCTO resulted in dense microstructure of the sample, which could possess excellent

Figure 13: (a) TEM image of an isolated $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano-dot. (b) SAED pattern of nano-dots (c) Corresponding energy dispersive X-ray analysis (EDX) spectrum [43].

Figure 14: AFM measurement of nano-powders calcined at 800°C for 3 h $\text{CaCu}_3\text{Ti}_{4-x}\text{Zr}_x\text{O}_{12}$ ($x = 0.02, 0.10, 0.20$ and 0.50 mol%) [44].

electrical properties. Formation of barrier layers and presence of interfacial polarization gave rise to increased value of the dielectric constant. The effect of doping Zr [$x = 0.02, 0.1, 0.2$ and 0.5 mol%] on the dielectric constants of samples sintered at 1020°C and 1040°C are shown in Figure 15 (a & b).

The high dielectric constants of these samples are 2960, 4190, 4610 and 6770 and the corresponding dielectric losses are 0.5, 1.0, 1.0 and 1.0. The results show that the highest dielectric constant at 50 Hz is achieved when the dopant concentration is 0.5. In the case of ceramic sintered at 1040°C it may be observed that the highest dielectric constant is obtained when the concentration value of x is 0.1. According to these results zirconium with $x = 0.1$ gives high dielectric constant 12,700 and low dielectric loss of 3.0.

Xu et al. [45] prepared Zn-substituted $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics by the sol-gel method using the precursors of $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$,

Figure 12: HRSEM microstructures of $\text{CaCu}_3\text{Ti}_{4-x}\text{Co}_x\text{O}_{12}$ [$x = 0, 0.02, 0.1, 0.2, 0.5$ and 1.0] respectively [41].

Figure 15: Effects of zirconium doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics on the dielectric constant sintered at 1020 and 1040°C [44].

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$. XRD analysis indicated that $\text{CaCu}_{3-x}\text{Zn}_x\text{Ti}_4\text{O}_{12}$ (CCZTO) ($x = 0.00, 0.06, 0.10, 0.20$) ceramics, after sintering at 1050°C for 20 h, consisted of a single phase, with no secondary phases. SEM results indicated that the samples had smaller grain sizes than those synthesized by traditional solid-state reaction methods and also found that some ZnO grains appeared on the grain boundaries in $\text{CaCu}_{2.9}\text{Zn}_{0.1}\text{Ti}_4\text{O}_{12}$ and $\text{CaCu}_{2.8}\text{Zn}_{0.2}\text{Ti}_4\text{O}_{12}$, which led to grain confinement in the CCTO. From the dielectric measurements it was found that $\text{CaCu}_{2.94}\text{Zn}_{0.06}\text{Ti}_4\text{O}_{12}$ (the sample with $x = 0.06$) had the best properties, with the highest nonlinear coefficient, the lowest threshold field, a high dielectric constant and a low dielectric loss factor at frequencies below 10^5 Hz. These properties make it a candidate for applications in low voltage varistor switchings, gas-sensing devices and varistor-capacitor double property devices.

Banerjee et al. [46] has prepared the giant dielectric material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) through a simple, cost-effective, environment friendly and energetically beneficial 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 pathway yields phase-pure and impurity-less CCTO ceramic at an ultra-low temperature (700°C) and is better than those obtained by the traditional solid-state reaction. From the X-ray diffractograms it is evident that the powder calcinated at 700°C has the proper $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ phase. On microscopic investigation, the matrix using SEM and TEM were seemed to be nano-crystalline and highly porous with pore sizes in the range of ~ 0.1 – 1.5 μm . 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.

Wang et al. [47] employed the sol-gel method to synthesize pure and Nd doped $\text{Ca}_{(1-3x/2)}\text{Nd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ($x = 0, 0.1, 0.2$ and 0.3) ceramics. XRD patterns show that NCCTO ceramics (sintered at 1,000°C for 6 h) were single phase with no Cu-rich phase. The lattice parameters show an increasing trend with the enhancing

amount of Nd^{3+} substitution. SEM picture in Figure 16 reveals that particlesize monotonously decreases from 250 to 120 nm with increase of Nd concentration. The average grain size of CCTO ceramics decrease from 2.0 to 0.8 μm with increase in Nd doping, which indicates that high concentration of Nd inhibits grain growth of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Both the dielectric constant and dielectric loss decrease with increase in Nd concentrations. $\text{Ca}_{(1-3x/2)}\text{Nd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics with $x = 0.3$ shows the lowest dielectric constant of 1.12×10^4 as well as the lowest dielectric loss value of 0.12 at 20 °C (10 kHz). This is due to high concentration of Nd concentration on planar defects in CCTO which could increase the electrical resistivity of the internal barrier and decrease the dielectric loss.

Sang wong et al. [48] successfully synthesized the nano-crystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders by a polyvinyl pyrrolidone-dimethyl-formamide (PVP-DMF) solution route. XRD showed that pure phase of CCTO was achieved at a low calcination temperature and short reaction time at 800°C for 3 h. TEM images of powders calcined at 700 and 750°C for 3 h with crystallite size of about 100 nm. The crystalline particles with necking growth of grains are clearly observed in this sample with the crystallite size in the range of ~ 200 – 500 nm. The sintered CCTO ceramics exhibited very high dielectric constants of about 12,590 and 37,685 for the ceramics sintered at 1050°C for 3 and 12 h, respectively. The nonlinear current-voltage behavior is closely related to the microstructure of CCTO ceramics.

Spray pyrolysis: Another solution-based approach in the synthesis of ABO_3 perovskite type $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and its isomorphs is spray pyrolysis which is an effective technique for obtaining the CCTO powders with fine size and regular morphology. The starting solutions can be sprayed ultrasonically or peristaltically into the high-temperature reactor by a carrier gas. The precursor solution can be made by dissolving stoichiometric amounts of calcium nitrate, copper nitrate and water soluble Ti-oxynitrate.

Figure 16: SEM images of (a) CCTO (b) NCCTO $x=0.10$ (c) NCCTO $x=0.20$ (d) NCCTO $x=0.30$ [47].

Liu et al. [49] synthesized CCTO by pyrolyzing an organic solution containing stoichiometric amounts of the metal cations in a stable solution prepared by dissolving calcium nitrate, copper(II) nitrate, and titanium(IV) isopropoxide in 2-methoxyethanol. This solution was pyrolyzed and heat-treated to achieve single-phase CCTO, which is done at lower temperature and shorter reaction time than the conventional solid-state reaction. The X-ray diffraction analysis showed that the sample heated at 700 °C for 2 h produced the CCTO at a much lower reaction temperature and shorter time than those required for the solid-state reaction, i.e., 1000 °C for 20 h. The SEM analysis shows grain dimensions in the 200–400 nm range which increase to 2–3 µm after being cold-pressed into pellets and sintered at 1050 °C for 4 h. The dielectric behavior of the sintered sample is similar to that of CCTO made by solid-state reaction with its dielectric constant 11500 independent of frequency and temperature below the relaxation frequency.

Liu et al. [50] have also synthesized CCTO using two wet-chemistry methods, namely, combustion method and the pyrolysis method at relatively low temperature and short heat treatment duration using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $[\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4]$, anhydrous citric acid, acetylacetone, 2,4-pentanedione and anhydrous ethylene glycol. In both methods, the metal oxides are formed in the first heat treatment step and CCTO is produced by a subsequent solid state reaction. X-ray diffraction analysis shows that the sample prepared by combustion method treated at 800 °C for 2 h, has pure CCTO, with no detectable impurities and sample synthesized by pyrolysis method produced the CCTO pure phase at 800 °C for 1 h without any secondary phase. Scanning electron microscopy (SEM) of the combustion method sample after sintering for 4 h at 1030 °C, showed that the grain sizes have a narrow distribution in the range of 0.4–1.0 µm. The sample produced by pyrolysis method and sintered at 1030 °C, has particle dimensions in the range of 0.5–1.5 µm, which is a little larger than those obtained by the combustion method while dielectric behaviors of both samples are similar. Specifically, they all have a Debye-like relaxation with a steep decrease in ϵ' at the frequency where ϵ'' displays a relaxation peak. At -150 °C and 113.38 Hz, the measured dielectric constant of sample obtained by combustion method is 159330 and that of sample by pyrolysis is 39008. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has a giant dielectric constant up to 10^5 at room temperature and great potential for technological application.

Swatsitang et al. [51] successfully prepared $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanoparticles by a simple polymer pyrolysis method. The XRD results show that both of the calcined powders at a low temperature 800 °C (CCTO-1) and 850 °C (CCTO-2) in air for 4 h have pure perovskite structure. The crystallite sizes, as evaluated by the XRD line broadening technique are 47.5 and 75.0 nm, respectively. The particle sizes as estimated from the bright field images of TEM were found to be in the range of 10–35 and 7–52 nm for CCTO-1 and CCTO-2, respectively, and are shown in Figure 17.

The dielectric measurement of the pellet sintered at 1,050 °C in air for 6 h (CCTO-2A) having the values of dielectric constant

(ϵ') and the low loss tangent ($\tan\delta$) at 1 kHz and 20 °C were found to be 11,472 and 0.0438, respectively, at this temperature. The giant dielectric constant and $\tan\delta$ values are suggested to be closely related to its microstructural density, calcination temperature and the Maxwell–Wagner polarization.

Precipitation method: The solution-based methods offer the advantages of optimum particle size and phase purity. Barbier et al. [52] studied the electrical properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ -based pellets and thick films obtained from the similar raw precursor prepared by the co-precipitation method. The metal chlorides (CaCl_2 , TiCl_3 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) were dissolved in water and then poured in ethanol-containing oxalic acid used as the precipitating agent. In order to obtain oxide powders, these precursors were calcined in air at 950 °C for 10 h and the dielectric characteristics of pellets and thick films were compared. The pellets exhibit high values of the dielectric permittivity ($\epsilon_r \sim 1.4 \times 10^5$) and relatively small dielectric losses ($\tan \delta \sim 0.16$) at 1 kHz and room temperature. CCTO thick films present very high values of their dielectric permittivity ($\epsilon_r \sim 5 \times 10^4$) even if they are lower than the one of the CCTO pellets. From a physical point of view the difference in copper content and grain size, and possibly various oxidation states may explain the changes in the dielectric permittivity between films and pellets. This result, which is

Figure 17: Low resolution TEM images of the CCTO-1 (a) and CCTO-2 (b) powder samples. Insets (a-1, b-1) and (a-2, b-2) are the high resolution TEM images and SAED of the CCTO-1 and CCTO-2 powder samples, respectively [51].

strongly related to the nature of the dielectric material in between the electrodes, constitutes a strong indication that the high dielectric permittivity values observed in this material are not related to an interfacial (electrode material) related mechanism but is an internal barrier layer capacitor (IBLC) type.

Thomas et al. [53] developed a wet chemical method for the preparation of complex oxalate precursor, $\text{CaCu}_3(\text{TiO})_4(\text{C}_2\text{O}_4)_8 \cdot 9\text{H}_2\text{O}$ which gives rise to nano-crystalline phase pure $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) powders with a crystallite size varying from 30 to 200 nm when heat treated at 680°C. The phase singularity of the complex oxalate precursor is confirmed by the wet chemical analyses, X-ray diffraction, FT-IR and TGA/DTA analyses. The UV-vis reflectance and ESR spectra of CCTO powders indicate that the Cu(II) coordination changes from distorted octahedra to nearly flattened tetrahedra (squashed) to square-planar geometry with increasing annealing temperature. TEM images of the phase-pure CCTO powders obtained from the thermal decomposition of the oxalate precursor at 700–900°C (Figure 18), reveal apparent micro-structural features (Figure 18 a–c). There are particles with curved (Figure 18d) edges and corners. The particles are weakly agglomerated (Figure 18d).

The micro-structural features as revealed by the HRTEM in nano-scale indicate that CuO_4 groups with the squashed tetrahedral geometry are more prevalent in the exterior regions of the powder particles as compared to the predominance of square-planar CuO_4 in the interior. The powders derived from the oxalate precursor have excellent sinter ability, resulting in high-density ceramics which exhibited giant dielectric constants up to 40,000 (1 kHz) at 25°C, accompanied by low dielectric loss 0.07.

Marchin et al. [54] synthesized the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ oxide by the

Figure 18: TEM images of phase-pure CCTO obtained at 680°C (a–c) and (d) weakly agglomerated particles (curved edges and corners) [53].

oxalate precursors. Oxalate precursors are obtained by the co-precipitation of calcium, copper and titanium chlorides with oxalic acid. XRD analysis reveals that the co-precipitation method allowed to obtain and to control the partition of several phases in addition to pure CCTO. The amount of these phases is simply controlled by varying the ratio of the reactants introduced during the synthesis. The SEM micrographs of the precursor powders reveal a disc-like morphology with an average diameter of 2–3 μm and a thickness of 300–400 nm. After decomposition, the oxide powders are obtained in homogeneous grains shape with size ranging from 0.2 to 1 μm.

Zhao et al. [55] synthesized the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders by basic co-precipitation method at 1100 °C for 10 h using polyethylene glycol (PEG) as suitable capping agent during co-precipitation procedure. SEM images of the precursor and calcined CCTO containing different amounts of PEG. Quasi-spherical CCTO powders with uniform diameter distribution of about 0.5–1.0 μm, regardless of small trails of agglomeration, were obtained without PEG dispersant. With the addition of PEG, CCTO powders arranged in a certain direction and the grain size became smaller, about 100–200 nm. The mechanism of the unique architectures formation maybe attributed to the role of PEG in growth rates control of different crystal faces through adsorption and desorption. The value of dielectric constant for samples containing PEG are smaller than pure CCTO because of small and in homogeneous grain size and permittivity shows little frequency dependence from 1000 to 10^5 Hz while the pure CCTO ceramics decreases sharply with frequency below 10^4 Hz, especially in the range of 100– 10^3 Hz.

Sen et al. [56] successfully synthesized single-crystalline CCTO nanostructures for the first time by a novel and convenient molten salt route. Calcium acetate, copper acetate, titanium dioxide (anatase) were taken as the precursors for CCTO while NaCl–KCl mixture (1:1 molar ratio, m.p.: 657°C) was used as the reaction medium. The technique is not only blessed with high yield but also can readily generate a wide range of morphologies from nano-particles, nano-cubes to nano-rods in reproducible way. XRD pattern of the sample synthesized at 800°C for 5 h were identical CCTO phase. The phase and morphology of the resultant products are sensitive to both reaction time and to the ratio of CCTO precursors to mixed chlorides. By minor adjustment of the controlling parameters, single-crystalline CCTO nano-structures can be obtained. The synthesized nanostructures, irrespective of their shapes, maintain single-crystalline character as it is evident from high-resolution transmission electron microscopic studies.

The present study will pave the way for the development of single-crystalline multi-component perovskite nano-structures, which were seem to be extremely hard to realize to date and expect our pathway to open up new direction for the synthesis of other multi-functional perovskite oxides single-crystalline nanostructures.

Hydrothermal processing: Hydrothermal synthesis is generally defined as crystal synthesis or crystal growth under high temperature and high pressure water conditions from substances which are insoluble in ordinary temperature and

pressure (<100°C, <1 atm). The critical temperature and pressure of water are 374°C and 22.1 MPa, respectively. The solvent properties for many compounds, such as dielectric constant and solubility, change dramatically under supercritical conditions [57]. There are only few reports on hydrothermal process because sintering temperature of CCTO required $\leq 1100^\circ\text{C}$ to produce single phase.

Keat et al. [58] synthesized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ using hydrolysis and subsequent condensation into a hydrous TiO_2 gel which was obtained by adding $\text{C}_4\text{H}_9\text{OH}$ diluted $\text{Ti}(\text{OC}_4\text{H}_9)_3$ drop-wise into water under stirring. Peptization was done by adding appropriate amounts of HNO_3 to form a translucent 0.4 M TiO_2 sol with a solution of pH of 1. Appropriate amounts of $\text{Ca}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ were then added in it. Due to the differences in the solubilities of the Ca, Cu and Ti, initial variations from ideal stoichiometry and a high solution pH was necessary to obtain stoichiometric $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ precipitates. The precipitate was sintered at 850°C and XRD peaks corresponding to the cubic CCTO phase were observed. The microstructures of the sintered CCTO, after polishing and thermal etching, the grain size estimated via automated image analysis was $0.7969\ \mu\text{m}$ while the circular intercept method shows the grain size to be approximately $0.8623\ \mu\text{m}$ which was in the submicron range.

Semi wet method

Singh et al. [59] synthesized nano-structured $\text{CaCu}_{2.90}\text{Zn}_{0.10}\text{Ti}_4\text{O}_{12}$ (CCZTO) electro-ceramic by semi-wet route and the pellets were sintered at 950°C for 6 h, 8h and 12h in air. The ceramics exhibit high dielectric constant of 1.35×10^4 at 1 kHz. The crystallite size of the CCZTO ceramic, obtained by XRD using Debye Scherer formula, range from 38-74nm which is in good agreement with the particle size observed by TEM analysis. It was observed clearly that the grain size significantly increased with an increase in sintering duration. Dielectric constant increases with increasing sintering time and dielectric loss decreases. It is suggested that the longer sintering time may lead to more defect structures. The increase in particle size with increasing sintering time is shown in Figure 19. It is mainly due to formation of large size particles as a result of loss of grain boundaries of small size particles. These changes lead to stability to the large size particles due to loss in grain boundary.

Singh et al. [60] studied the effect of doping Mg^{2+} at Cu^{2+} site in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ synthesized by modified sol-gel route using solid TiO_2 powder. XRD analysis confirmed the formation of single-phase material, and the structure did not change on doping of Mg and it remained cubic similar to $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO). The average particle size in sintered powder of the ceramic obtained from XRD and transmission electron microscopy (TEM) was found to be $59 \pm 05\ \text{nm}$ and $90 \pm 25\ \text{nm}$, respectively.

SEM image shows the presence of bimodal grains while EDX analysis confirmed copper oxide rich phase at the grain boundary. An exceptionally very high dielectric constant 86,084 at 500K on partially substituted Mg^{2+} at Cu-site in CCTO ceramic at 1 kHz was observed. The nature of relaxation behavior of the ceramic was also rationalized by impedance and modulus spectroscopic

Figure 19: TEM images of $\text{CaCu}_{2.90}\text{Zn}_{0.10}\text{Ti}_4\text{O}_{12}$ ceramics sintered at 950°C for (a) 6h (b) 8h and (c) 12h [59].

analysis. Modulus spectroscopic studies confirmed the Maxwell-Wagner relaxation arising due to the interfaces between grain and grain boundary.

Mandal et al. [61] studied the effect of doping at Ti^{4+} site by Ce^{3+} using $\text{CaCu}_3\text{Ti}_{3.90}\text{Ce}_{0.10}\text{O}_{12}$ synthesized by citrate-gel route. DTA/TG analysis of dry powder gives pre-information about formation of final product around 850°C . XRD analysis confirmed the formation of $\text{CaCu}_3\text{Ti}_{3.90}\text{Ce}_{0.10}\text{O}_{12}$ phase of the ceramic sintered at 950°C for 12hrs. Microstructure studied using Scanning Electron Microscopy (SEM) confirmed the average grain size in the nano range, 200 nm – 400 nm (Figure 20). The nature of relaxation behavior of ceramic was also rationalized using the impedance and modulus spectroscopy. While the bulk conductivity indicates an Arrhenius-type thermally activated process, the ac conductivity spectrum obeyed the Jonscher power law. The complex impedance diagrams of the ceramic exhibited a significant contribution from the grains, grain boundaries and electrode. The activation energies calculated from the grain-boundary relaxation time constant was found to be 0.49 eV which confirmed the Maxwell-Wagner type of relaxation in the ceramic.

Singh et al. [62] synthesized nano-crystalline electro-ceramic $\text{sCaCu}_{2.90}\text{Zn}_{0.10}\text{Ti}_4\text{O}_{12}$ (CCZTO), by solution-wet route (SR) as well as semi-wet route using citric acid (SWR1) and Glycine (SWR2) separately, and were characterized by TGA/DTA, XRD, TEM, SEM and EDX techniques. The crystallite size of the ceramics obtained by XRD were found to be in the range of 45–90 nm in good agreement with those observed by TEM analysis shown in Figure

Figure 20: SEM micrograph of $\text{CaCu}_3\text{Ti}_{3.90}\text{Ce}_{0.10}\text{O}_{12}$ sintered at 950°C for 12 h [61].

21. The grain sizes for the ceramics SWR1, SWR2 and SR observed by SEM were found to be in the range of $10\text{--}15\text{ }\mu\text{m}$, $1\text{--}4\text{ }\mu\text{m}$, and $2\text{--}4\text{ }\mu\text{m}$, respectively. Thermal studies show that the single phase CCZTO ceramic was formed in single step combustion reaction in SWR2 while in the case of SWR1 and SR they were obtained in multi-step reactions. SWR2 route shows more effective solid state reaction for the formation of nano-crystalline CCZTO single phase at much lower sintering temperature.

Singh et al. [63] also studied the ultrafine powders of $\text{CaCu}_{2.80}\text{Zn}_{0.20}\text{Ti}_4\text{O}_{12}$ synthesized by the novel semi-wetroute using metal nitrate solution and solid TiO_2 powder. DTA/TG analysis of dry powder gives pre-information about formation of final product around 800°C . Single-phase formation was confirmed by XRD sintered at 950°C for 12h which is much lower temperature compared to conventional ceramic method. The particle size of the ceramic was found in the nano-size range. The average particle size of sintered powder of the ceramic obtained from XRD and Transmission electron microscopy in Fig. 22 was found to be 59 nm and 102 nm, respectively.

Energy Dispersive X-ray studies confirm the stoichiometry and purity of the synthesized ceramic. The value of dielectric constant and dielectric loss of the ceramic was found to be 2031 and 0.353, respectively, which are nearly temperature independent at 100 kHz.

Conclusion

The urgent demand for high dielectric constant ceramic capacitors has been a key issue leading to the development of capacitor technology. In view of this the scientists and technologists have shown potential interest to obtain $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and its cation substituted isomorphs with high dielectric constant and low loss values. The critical success of new CCTO materials lies in their preparation which controls the morphology, particle size and its dielectric properties. In order to obtain these features, small particle size, narrow size distribution, uniform morphology, optimum crystallinity degree, high specific surface area, minimum defects and agglomeration, and homogeneous metal doping are required for the practical applications of

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders in capacitor. The only limitation which restricts the broad applications of this compound is the dielectric loss. Methods described in this overview were designed to obtain $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano-crystalline powders with desired structures and high dielectric constant. Since the number of surface atoms or ions becomes a significant fraction of their total number, and the surface energy plays an important role in the thermal stability and crystal structure, the materials in the nanometer size range exhibit some remarkable properties which can be exploited to get high dielectric constant and low loss CCTO.

Figure 21: TEM images of (a) SWR1 (b) SWR2 and (c) SR synthesized by diverse routes sintered at 950°C for 12h [62].

Figure 22: TEM image of $\text{CaCu}_{2.80}\text{Zn}_{0.20}\text{Ti}_4\text{O}_{12}$ sintered at 950°C for 12 h. [63].

Although solid-state synthesis is an established conventional route to obtain well-crystallized particles of CCTO with ordered structure, it requires high treatment temperature and longer process time leading to larger particle size and high dielectric constant and low dielectric loss. Uncontrollable particle growth and agglomeration, associated with solid-state synthesis can be partially suppressed using sol-gel methods. However, there is a need for new synthetic methods which reduce energy consumption, cost, and processing time. The solution chemistry methods with focus on sol-gel method and basic co-precipitation synthesis give high purity, small particle size, uniform size distribution, and hence desirable dielectric properties. Most probably the sol-gel method which is highlighted in this overview may develop into a commercial viable approach to the production of large scale CCTO nano-crystalline powders for use in device applications. Several methods have been reported by various researchers to prepare nano-size CCTO and similar ceramic with high dielectric constant. Among these the most adopted solid state reaction method lacks in terms of homogeneity of precursor materials. In addition, the process requires higher sintering temperature and longer sintering time for solid state diffusion to occur for single phase-formation. Wet chemical synthesis routes, such as sol-gel, hydrothermal/solvothermal, or co-precipitation methods, have more advantages over solid-state reactions in achieving better homogeneity and mixing of the starting compounds on molecular level. The semi-wet method using aqueous metal nitrate solutions and solution of oxide of titanium along with oxalic acid as complexing agent at lower sintering temperature in shorter sintering time is the current approach for the synthesis of the best quality nano-CCTO and its isomorphs and similar ceramic materials.

Acknowledgement

Authors are grateful to Prof. Om Parkash, Department of ceramic Engineering, IIT (BHU) and Prof. R.K. Mandal, Department of Metallurgical Engineering, IIT (BHU) for their fruitful discussions on SEM and TEM analysis.

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