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Colossal dielectric constant and extremely low loss in T-type $La_2CuO_{4-\delta}$ ceramics

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ABSTRACT

In this paper, we present the colossal dielectric behavior of T-type $La_2CuO_{4-\delta}$ (LCO) ceramics synthesized in fine grained form using wet chemical "Pechini" process, followed by annealing in argon (Ar) atmosphere. The colossal dielectric constant (CDC) ($10^3 \leq \varepsilon_r' \leq 10^4$) displayed over a wide frequency (1 Hz $\leq f \leq$ 1 MHz) and temperature (-100–150 °C) ranges was equally complimented by the remarkably low dielectric losses ($0.01 \leq \tan\delta \leq 0.1$) for LCO ceramics, which are the lowest reported dielectric losses for the T-type La_2CuO_4 system, so far. This substantial decrease in losses could be attributed to the enhanced resistivity ($10^8 - 10^9$ Ω.cm) of the sample. Further, the origin of CDC, in this non-ferroelectric LCO, was investigated using combined ac impedance and modulus spectroscopy. The study revealed heterogeneity in electrical microstructure of LCO, with semiconducting grains and insulating grain boundaries. This electrically heterogeneous microstructure could give rise to the Internal Barrier Layer Capacitance (IBLC) mechanism, thus leading to apparent CDC in LCO.

1. Introduction

High dielectric constant materials are considered technologically important, as they could facilitate the miniaturization of various electronic devices. So far, only non-centrosymmetric, ferroelectric (FE) materials have been extensively investigated for this purpose [1,2]. However, recently few non-ferroelectric (NFE) materials viz. CCTO, nickelates (K_2NiF_4) have also displayed colossal dielectric constant and they are being studied for possible use in microelectronics [3–7]. These NFE materials show significant temperature independence over FE materials (wherein ε' vary abruptly at Curie temperature). However, these colossal dielectric, NFE materials are limited by their equally high dielectric losses. The reduction in the dielectric losses remains the biggest challenge in applicability of these NFE's over existing FE materials in microelectronics.

In the quest of exploring new colossal dielectric materials, parent compounds of cuprate superconductors have emerged as a new addition to the existing category of NFE high dielectric constant materials [8–11]. Amongst these, T-type La_2CuO_4 attracted much attention and was explored extensively for exhibiting superconductivity (after suitable aliovalent (viz. Sr, Ba) substitution at La site) seems quite interesting [12,13]. For, the pristine T-type La_2CuO_4, compounds are believed to be Mott insulators (charge transfer insulators) with very close, co-existing, superconducting and insulating phases together [14].

The electrical properties of polycrystalline La_2CuO_4 have also been found to be sensitive to the oxygen concentration, with studies revealing the superconducting behavior of oxygen rich La_2CuO_4 ceramics at low temperatures [15–17], with few cases of tetragonal (*sp. gp.* I4/mmm) T-type La_2CuO_4 phase showing metallic like behavior [18]. This sensitivity of oxygen concentration on the electrical properties is also found in the magnetic behavior; with oxygenated La_2CuO_4 (annealed in oxygen gas flow at 500 °C) exhibiting Neel temperature (T_N) at around –173 °C, while, the deoxygenated La_2CuO_4 (annealed in argon gas atmosphere) exhibiting T_N below 30 °C [15,19]. The resistivity of these La_2CuO_4 cuprates also changed substantially, depending on the heat treatment for the ceramics [18].

Considering these properties of LCO to have close insulator-metal/superconducting phase separation gap and the oxygen dependent electrical behavior, the dielectric properties of La_2CuO_4, were considered interesting and they were studied extensively in single crystals [15,20] as well as bulk ceramic form [14,21,22]. These studies were carried over a wide frequency (f) and temperature (T) ranges (1 Hz $\leq f \leq$ 9 GHz, 5 K $\leq$ T $\leq$ 300 K), revealing colossal dielectric constant (CDC) ($\varepsilon' \geq 10^3$) for variety of La_2CuO_4 samples with different oxygen content [20–26]. Although, studied over wide frequency range, the dielectric data on these cuprates was largely restricted below room temperature ($<$ 300 K); also, barring a few (only on single crystal) [19], there was hardly any

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impedance study on these La_2CuO_4 cuprates. Moreover, being a non-ferroelectric and centrosymmetric, such CDC ($\varepsilon_r' > 10^3$) appeared quite interesting and warranted further investigation of origin of such a large dielectric constant in T-type La_2CuO_4.

From reported literature so far, only stoichiometric La_2CuO_4 or the oxygen deficient $La_2CuO_{4-\delta}$ is known to show nonmetallic properties and is not a superconductor. Hence, in this paper, we aimed to study various electrical properties of oxygen deficient La_2CuO_4 ceramics. The primary objective was to verify the origin of colossal dielectric constant exhibited by $La_2CuO_{4-\delta}$ (LCO) using combined ac impedance and modulus spectroscopy, with possibility of applicability of IBLC effect, Maxwell Wagner relaxation and other external contributory factors to this apparent CDC of La_2CuO_4.

2. Experimental procedure

T-type La_2CuO_4 powders were synthesized in phase pure form using both, the conventional powder mixing followed by solid state reaction[14,21] and wet chemical citrate gel complexation "Pechini" process [27,28], to check the reproducibility and reliability of data.

In conventional ceramic synthesis process, the starting raw powders *viz*. La_2O_3 (preheated at 900 °C/12 h), CuO were weighed in stoichiometric proportions and mixed using agate mortar and pestle for ~2–3 h. The nominally mixed starting materials were then ball milled for 24 h for intimate mixing. This finely mixed powder was solid state reacted (SSR) at 950 °C/12 h at ambient atmosphere. The resulting SSR powder was ground and later taken for powder X-ray diffraction (XRD), using PANalytical X'Pert Pro diffractometer having incident X-ray wavelength CuK_α = 1.54056 Å, for phase identification. This cycle of mixing, solid state reaction and XRD analysis was continued till complete T-type La_2CuO_4 phase was realized. This usually took 2–3 cycles for complete T-type phase formation.

In wet-chemical citrate gel complexation "Pechini" process, the constituent oxides were weighed in stoichiometric proportion and were dissolved in dilute nitric acid (HNO_3) to form the corresponding nitrates. These nitrate solution of La and Cu were then mixed using magnetic stirrer and heated to 70 °C, with continuous stirring till a clear solution is formed. To this solution, enough citric acid concentrated solution and ethylene glycol were added to form citrate complexes. The pH of the solution was maintained strictly around 6.2 by addition of ammonia; during the pH change, color of the solution changes from sky blue to navy blue. Further heating of this solution to 120 °C made way for the formation of dark navy blue colored gel. To hasten the process of drying (xerogel formation), the gel was kept in vacuum oven at 150 °C. The dry mass of powder thus obtained, was calcined at 350 °C/2 h. This powder was ground in agate mortar and was heated in a furnace for 800 °C/6 h to realize the T-type phase formation, as revealed by powder XRD pattern. The advantage of using Pechini process is that, it facilitates the molecular level mixing of constituent atoms, thus giving better stoichiometry. Also, due to this, the SSR temperature can also be seen to reduce substantially (by 150 °C) as compared to the conventionally prepared ceramics. The particle size and morphology of the powders synthesized using Pechini's process was observed to be ≤ 100 nm, using (JEOL JEM-2100) high resolution transmission electron microscope (HR-TEM); while, the particle size of conventionally processed powders was determined using laser particle size analyzer (*viz*. Beckman Coulter LS 13,320); the mean volume particle size, through optimum grinding, was restricted to ~1 μm.

After the T-type phase confirmation by both these processes, and grinding the particles to suitable particle size through ball milling, the resulting phase formed, fine powders were compacted in thin pellet form of ~12 mm diameter and 1 mm thickness using uniaxial hydraulic press, exerting 100 MPa pressure. The pellets of La_2CuO_4 formed from conventionally prepared powders were sintered at an elevated temperature of 1100 °C/12 h, while those powders prepared from Pechini's process were sintered at much lower temperatures of 950 °C; also, the soaking temperature, as compared to the conventional ceramic process, was also reduced to half, 6 h.

Further, all these pellets were subjected to various annealing (Oxygen, argon, ambient) conditions in anticipation of change in the electrical properties. Along with this, the LCO samples were also synthesized by vapor doping method, in which extra CuO powder was kept in the vicinity of green LCO pellets while sintering, covered with the crucible. However, while readying the samples for capacitance measurement, by applying silver paste to opposite faces of the pellet, only oxygen deficient (Ar annealed) sample were found suitable for capacitance measurement, all other samples were found to get electrically shorted, indicating their metallic nature, which usually happens when sample are oxygen enriched [15,18]. The La_2CuO_4 ceramic samples were kept for Ar annealing at 900 °C for 10 h so as to have about 1% oxygen deficiency [15]. The microstructures of the ceramic samples were recorded using scanning electron microscope (SEM) (JEOL model No. JSM-7600 F; JEOL Ltd., Tokyo, Japan), elemental analysis of the phase formed samples was carried out using energy dispersive X-ray spectroscopy (EDX) attached to the SEM (Oxford instruments). The dielectric study over $La_2CuO_{4-\delta}$ (LCO) samples were carried over wide frequency (1 Hz $\leq f \leq$ 1 MHz) and temperature (−100–150 °C) ranges using Novocontrol broadband dielectric spectrometer (Alpha A analyzer), with BDS 1200 sample holder.

3. Results and discussion

3.1. Phase Purity of T-type La_2CuO_4

The phase purity of the T-type La_2CuO_4 ceramic samples synthesized using conventional powder mixing-ceramic sintering route with vapor doping [14], as well as the samples prepared using Pechini process, followed by argon annealing [15] was verified using powder X-ray diffraction technique (see Fig. 1). All the samples matched with orthorhombic T-type phase of La_2CuO_4 having *space group* Bmab and were indexed to the JCPDS file no. 01-082-2133 [21,29]. This orthorhombic (*sp. gp*. Bmab) is the most commonly occurring phase of La_2CuO_4 compound.[30,31].

The particle size and morphology of the conventionally as well as Pechini processed samples is shown in Fig. 2(a) and (b) respectively. The La_2CuO_4 powder prepared conventionally show bimodal particle size distribution, with particles consisting of finer (size of 0.75 μm) and coarser particles (1.8 μm). While, particle size of "Pechini" processed LCO powders analyzed using TEM, showed formation of hard agglomerate (Fig. 2(b)), with average particle size of ~ 100 nm with few coarser particle of ~150 nm (inset of Fig. 2(b)). The particles show nearly rounded morphology for powders prepared by both the methods, followed by ball milling. Fig. 3(a) shows the SEM photomicrograph of the La_2CuO_4 conventionally prepared sample, sintered at 1100 °C/12 h, enriched with oxygen by vapor doping method [14]. The SEM revealed a dense microstructure and uniform grain size distribution, with average grain size ($\bar{D}$) ≈ 5 μm. The vapor doping method has resulted in some segregated phase along the grain boundaries. To analyze this phase, backscattered SEM image was taken over the same area (see Fig. 3(b)), which revealed that the segregated phase belong to some other phase. The EDX (Fig. 3(d)) taken over this segregated phase (spectrum 1) confirmed that it is Cu and O