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Title: Study of Physical and Chemical Mechanism Responsible for Colossal Dielectric Phenomenon in Calcium Copper Titanate (CCTO)

FINDINGS

$CaCu_3Ti_4O_{12}$ (CCTO) samples have been synthesized by the Solid-state reaction technique, the Sol-gel technique and the Microwave flash combustion technique. These synthesis techniques have produced various crystallite size of CCTO such as i) micron by Solid-state reaction ii) nano by Sol-gel and iii) nano with rapid synthesis by microwave flash combustion. The synthesized CCTO powders have been sintered by conventional sintering, spark plasma sintering and microwave sintering. These sintering methods are fundamentally different. In the conventional sintering, the heat is transferred from the wall to the bulk of CCTO via heat conduction. In the microwave sintering, a self-sustainable heat is generated internally in the CCTO powders through the interaction of molecules with the electromagnetic field. In Spark plasma sintering; an electric discharge generates the plasma (an ionized gas) between the CCTO powder particles under the simultaneous application of mechanical pressure and high-power pulse. CCTO is chatecterized by XRD, TEM, SEM, EDX, density measurement, dielectric measurement and impedance spectroscopy.

Solid-state synthesized CCTO powder was sintered at 1050°-1100°C for 5-40 h with conventional sintering method. The density was observed from 86 to 96 % of the theoretical density, dielectric constant is found from 1500 to 34000 and grain size of sample was in 40-60 μm range. Microwave sintering was performed at 1000-1075°C for 15 min. In this sintering, the sintered samples have the average grain size of 8-12 μm, dielectric constant of ~ 6800 and loss tangent of ~ 0.12. Further, Spark plasma sintering of calcined CCTO powders was carried out at 1050 ºC for 15-60 min under the pressure of 50 MPa. Dielectric permittivity was observed to 2.0×10^6. The

resistance at the grain and grain boundary are 10 Ω and 190 Ω which are calculated by impedance spectroscopy.

Sol-gel derived nanocrystalline (50-100 nm) CCTO powders were sintered conventionally at 1025°C for 5 h. These samples have dielectric constant of 5000 and loss tangent of 0.37 at 10 Hz. Microwave sintered CCTO nanocrystals was sintered at 1050-1075 °C for 15 min, and its dielectric constant was ~ 2900 and loss tangent of ~ 0.17 at 10 Hz. Spark plasma sintering of calcined CCTO nanocrystals was performed 1050 °C for 5 min. Dielectric constant and loss tangent at 10 Hz was 28000 and 1.2, respectively. The grain and the grain boundary resistance were calculated to be 20 Ω and 450000Ω. The activation energy of this electro-conduction was measured to be 0.495 eV.

Microwave flash combustion synthesis of nanocrystalline (50-100 nm) CCTO was carried out by microwave irradiating (2.45 GHz and 1.1 kW power). Convetional sintered (at 1050°C for 5 h) shows that the dielectric constant of 20000 and loss tangent of 0.51 at 100 Hz, respectively. The grain and grain boundary resistance were calculated to 40 Ω and 8 MΩ, respectively. Microwave sintering of calcined CCTO nanoparticles was carried out at 1075°C for 15 min. Its dielectric constant and loss tangent are 52800 and 0.2 at 100 Hz. Using Cole-Cole plots, the grain and grain boundary resistance were calculated to 10 Ω and 360000Ω, respectively. Its activation energy was calculated 0.58 eV. Further, Spark Plasma sintering was performed at 1050°C for 5 min. Sintered samples have the dielectric constant of 20000 and the loss tangent of 5.5 at 100 Hz. An electrically heterogeneous microstructure is confirmed by impedance spectroscopy as the grain and the grain boundary resistances were found to be 10 Ω and 32000Ω. The activation energy of grain boundary was calculated to be 0.478 eV.