Giant Dielectric Response in (Sr, Sb) codoped $CaCu_3Ti_4O_{12}$ Ceramics: A novel approach

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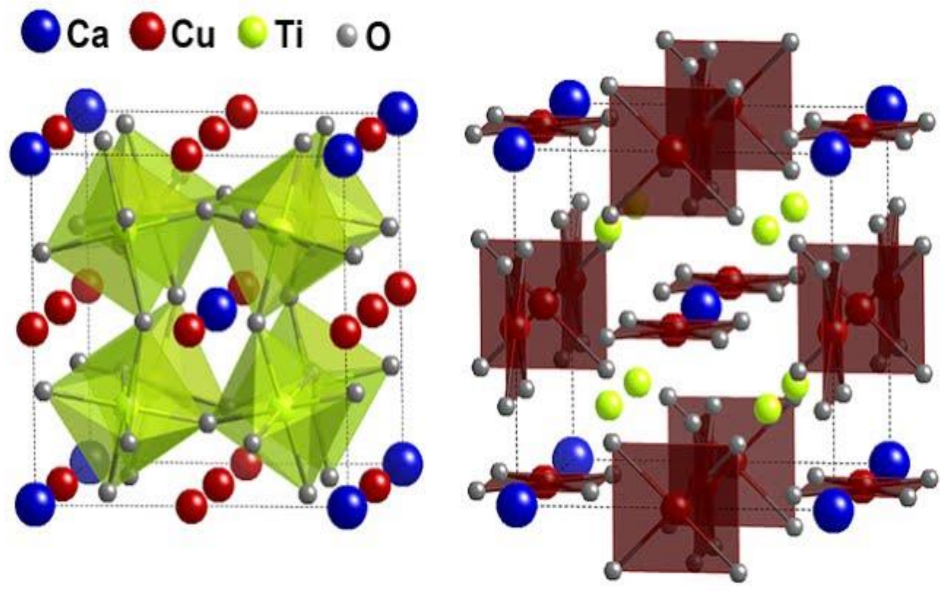
Abstract

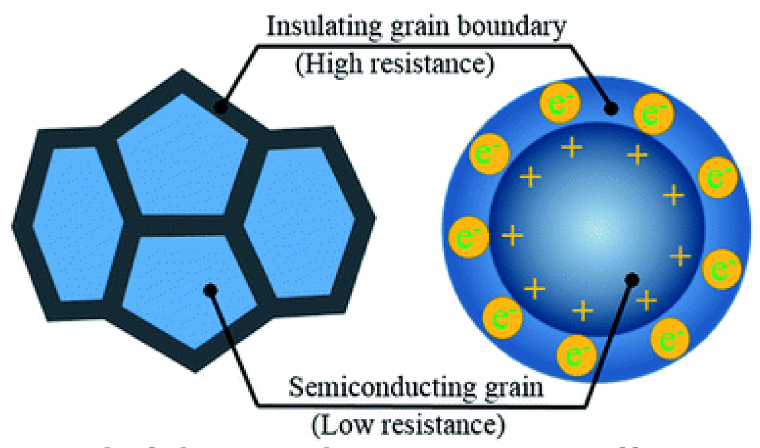
We report enhanced dielectric properties and dielectric relaxation behaviors of $CaCu_3Ti_4O_{12}$ (CCTO) by adopting a novel approach of codoping (Sr,Sb).Structural, microstructural and dielectric properties were investigated in details. Sr substituted in Ca site can effectively suppress the grain growth, further increase in Sb concentration as a codopant shows hike in dielectric constant. Dielectric properties of CCTO are explained in terms of a capacitive-layer model consisting of semiconducting grains and insulating grain boundaries.

Introduction

- Technological applications like supercapacitors and electronic devices rely on materials that possesses a high dielectric constant, low dissipation, temperature and frequency stability, energy density, charge-discharge cycles ,break-down voltage etc.



- It shows so called ''giant-dielectric phenomenon'' or "colossal "dielectric constant ~ 10^4,which is contrast to ferroelectrics.



- Internal barrier layer capacitor (IBLC) model based on Maxwell–Wagner polarization, relates colossal dielectric permittivity (ε) to the electrically heterogeneous microstructure.

Experimental

$CaCO_3$, CuO, TiO_2, $SrCO_3$, Sb_2O_5
Appropriate weights of starting materials
⇩
Homogeneous Mixing with Agate and Mortar
⇩
Calcined at 900°C,24hrs
⇩
Regriding of Calcined Powder
⇩
Powder Pressed into Pellet and Sintered at 1100°C, 24 hr

- **A series of samples prepared : $CaCu_3Ti_4O_{12}$ as CCTO, $Ca_{0.9}Sr_{0.1}Cu_3Ti_4O_{12}$ as CCTO1, $Ca_{0.9}Sr_{0.1}Cu_3Ti_{3.99}Sb_{0.01}O_{12}$ as CCTO2 and $Ca_{0.9}Sr_{0.1}Cu_3Ti_{3.95}Sb_{0.05}O_{12}$ as CCTO3.**
- **Investigation of Phase purity and microstructures by XRD(CuKα) and SEM(Jeol, USA)**
- **Coating pellets with silver paint and drying for Impedance Measurement using HIOKI3570 and homemade dieletric cell.**

Conclusion

- **Dielectric constant of modified CCTO achieved upto several orders by co-doping of Sr, Sb ions.**
- **Correlation between electrical behavior mainly dielectric relaxation and microstructure reveals that modification affects grain boundary resistance leading to high dielectric constant.**
- **Giant response is correlated with the potential barrier height at grain boundaries (GBs).**

References

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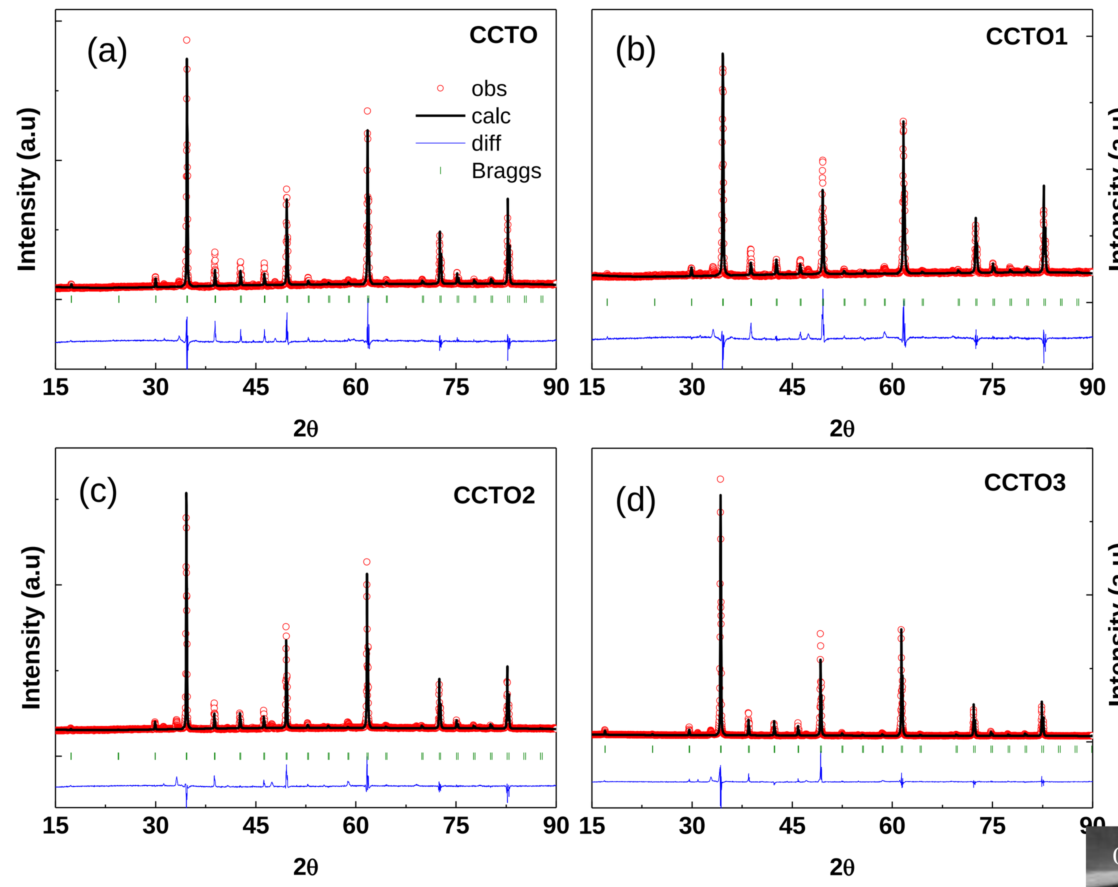
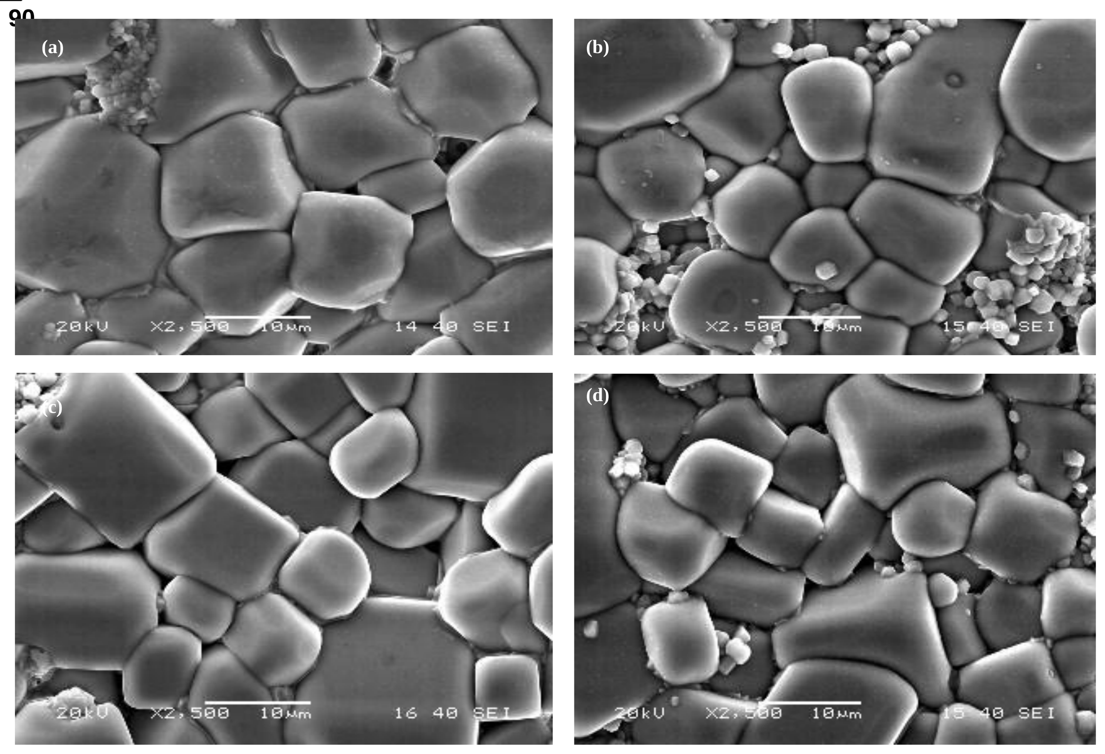
Results and Discussions

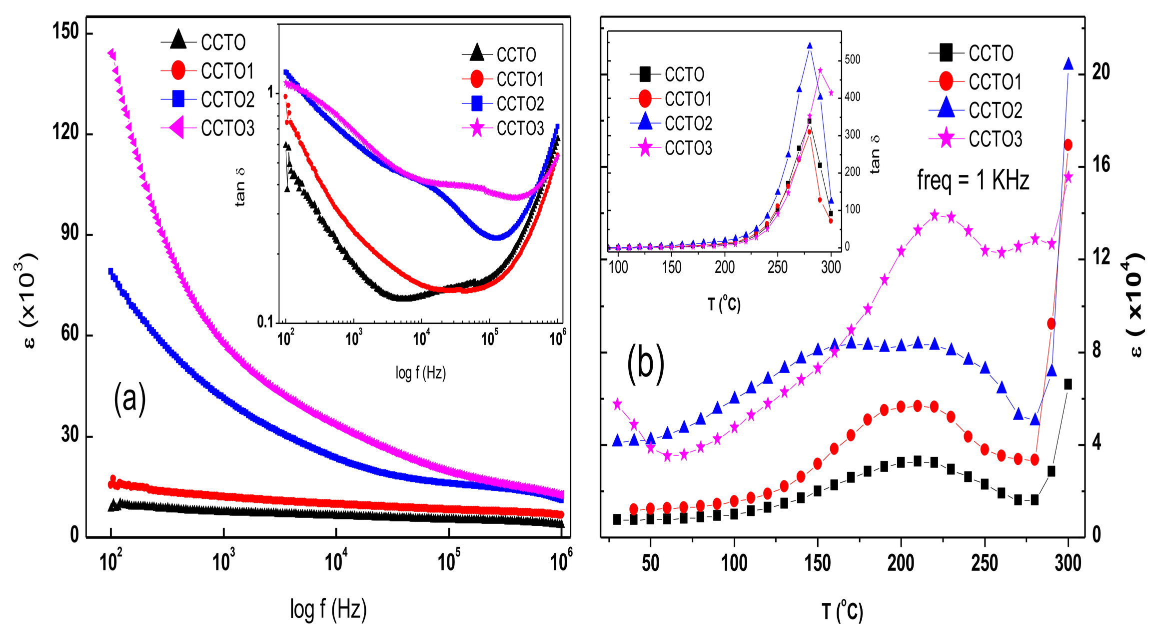


- Quantitative Phase analysis of XRD by Rietveld Method .
- The decrease in lattice parameter with Sr^{2+} and on various concentration of Sb^{5+} might be attributed to variations in ionic radii.

Elements	Wycof-symbol	CCTO	CSCTO (Sr=10%)	CSCTSO1 (Sr=10%, Sb=1%)	CSCTSO2 (Sr=10%, Sb=3%)	CSCTSO3 (Sr=10%, Sb=5%)
Ca/Sr	*x, y, z*	0,0,0	0,0,0	0,0,0	0,0,0	0,0,0
Cu	*x, y, z*	0,0.5,0.5	0,0.5,0.5	0,0.5,0.5	0,0.5,0.5	0,0.5,0.5
Ti/Sb	*x, y, z*	0.25,0.25,0.25	0.25,0.25,0.25	0.25,0.25,0.25	0.25,0.25,0.25	0.25,0.25,0.25
O	*x, y, z*	0.2949(5) 0.1810(5) 0	0.2829(4) 0.1773(6) 0	0.3044(2) 0.1663(3) 0	0.2987(6) 0.1866(1) 0	0.2991(7) 0.1863(1) 0
Cell parameter(Å)	*a*	7.4030(9)	7.4023(2)	7.3958(8)	7.4058(4)	7.3979(4)
Volume($Å^3$)	v	405.724	405.303	404.534	406.193	404.895

- **Mean grain sizes of CCTO, CCTO1, CCTO2 and CCTO3 were found to be 15.61, 12.08, 18.21, 10.04 μm, which indicates the effect of co-doping of Sr and Sb in the microstructure of CCTO.**
- **SEM micrograph shows microstructure has highly compacted grains with grain boundaries.**





- **At low frequency a gigantic change in the permittivity of CCTO3 occurs as compared to the pure CCTO.**
- **Frequency dependence of tanδ shows two relaxations, corresponding to DC conduction and primary polarization respectively.**

- **One major semicircular arc in all the plots depicts the presence of grain-boundary effect as the major contributor towards the characteristic dielectric behavior of these ceramics.**
- **Radii of semi-circular arcs at a particular temperature varies on modifications ,which may be a consequence of variation in the resistance of grain boundaries.**
- **Activation energy (E_a) of relaxation calculated to be 0.247eV, 0.258eV, 0.186eV and 0.203eV for CCTO, CCTO1, CCTO2 and CCTO3 respectively.**