Colossal Permittivity La-SrTiO₃ Ceramics for Base Metal Multilayer Ceramic Capacitors: Strategies for Reducing Sintering Temperature and Enhancing Dielectric Properties

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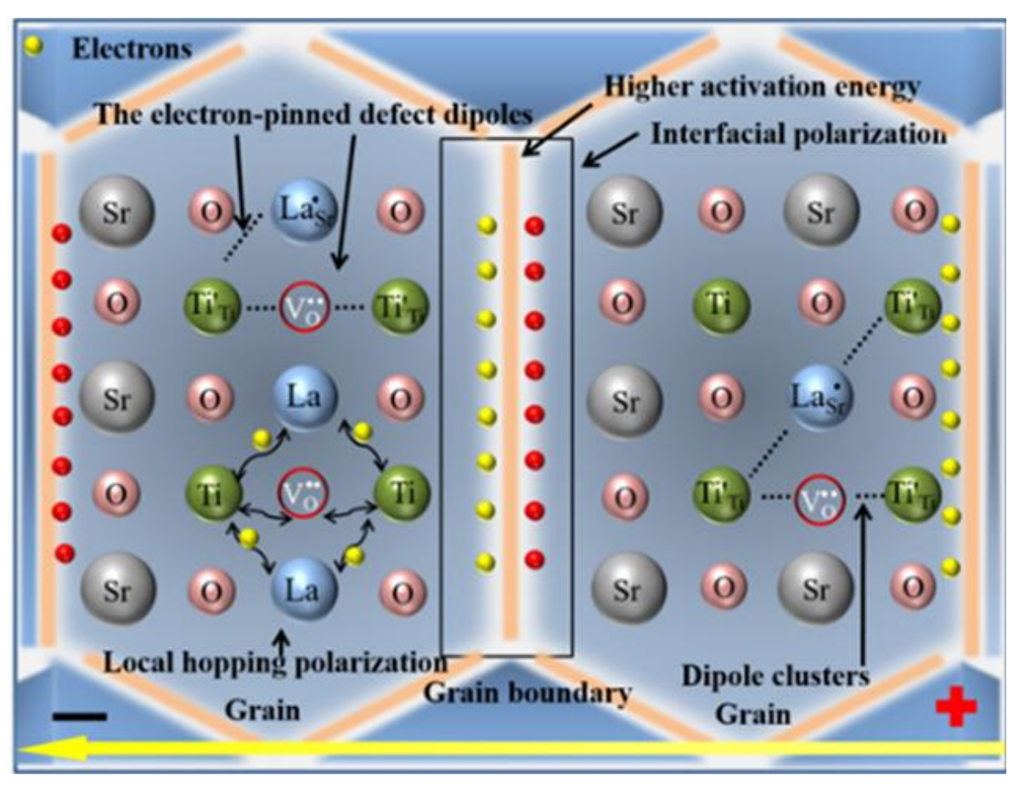
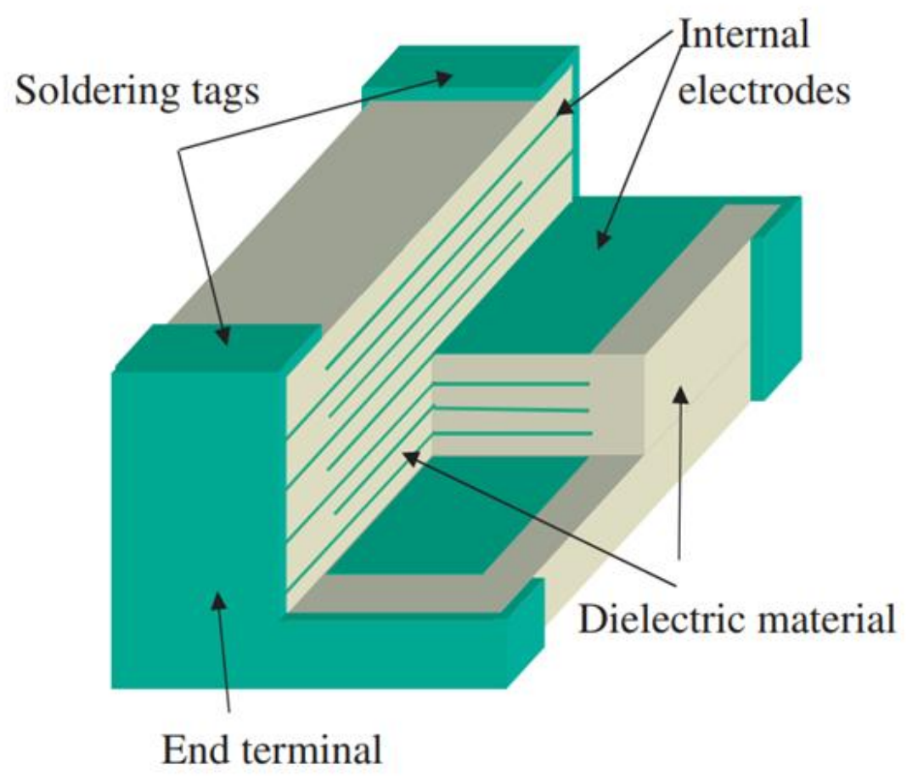
Introduction

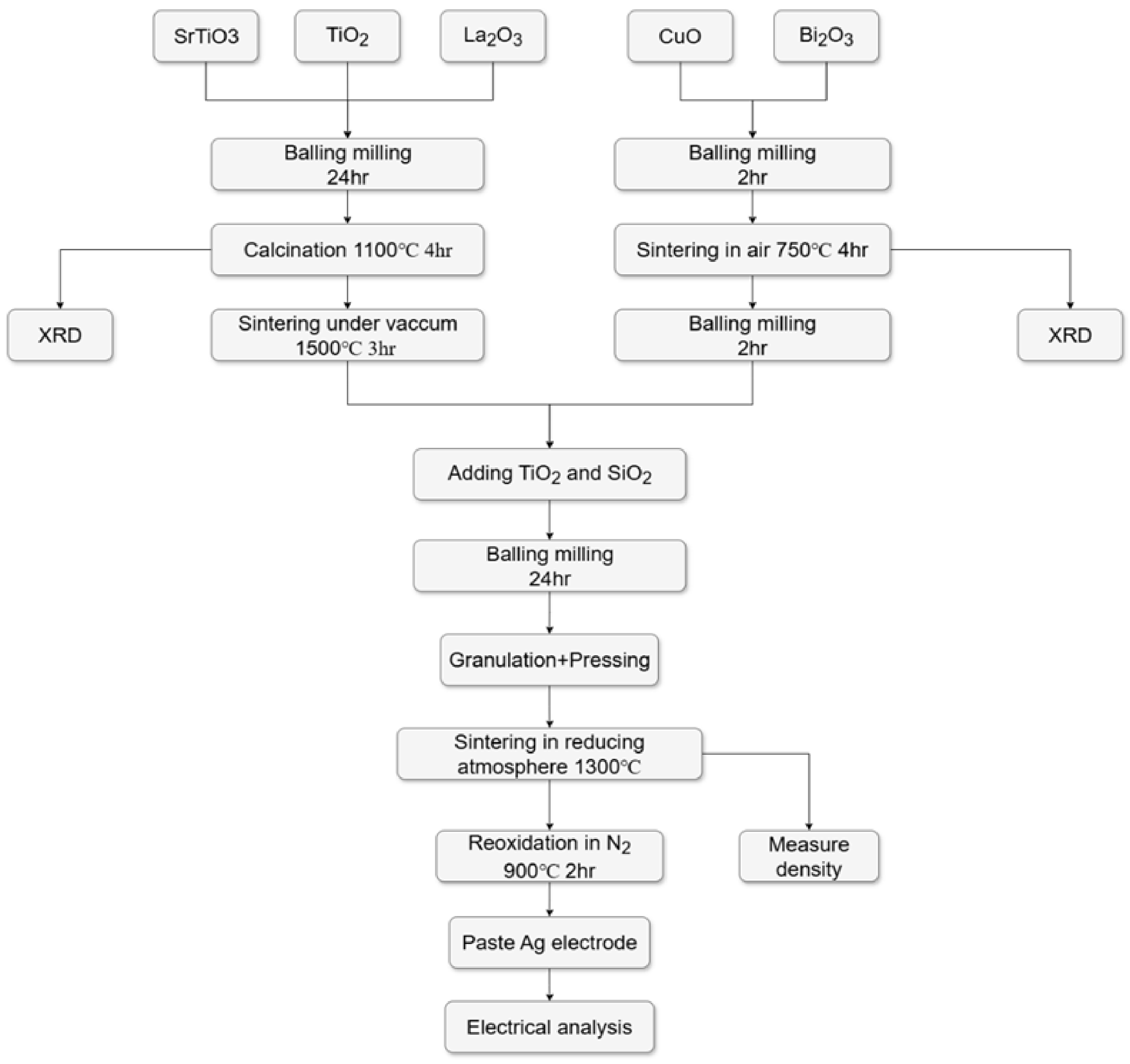
Multilayer ceramic capacitors (MLCCs) are composed of alternately stacked dielectric layers and internal electrodes, which are categorized into precious metals (Pd, Pt) and base metals (Ni, Cu). Considering cost, Ni is commonly employed as the internal electrode; however, its relatively low melting point (~1455 ˚C) is incompatible with the high-temperature, low-oxygen-partial-pressure conditions required for sintering colossal dielectric materials, resulting in difficulties in co-sintering. To address this issue, this study adopts liquid phase sintering (LPS), in which appropriate additives are introduced to reduce the sintering temperature, thereby preventing Ni melting and dielectric layer degradation. In addition, acceptor doping is employed to regulate grain boundary charge balance and oxygen ion diffusion, optimizing the distribution of oxygen vacancies, suppressing dielectric relaxation, and enhancing the Schottky barrier as well as the insulation resistance.

According to previous studies, electron-pinned defect dipoles (EPDD) can be utilized to achieve both colossal permittivity and low dielectric loss. In this work, La was doped into SrTiO₃ to generate defect dipoles Ti'_{Ti}—$V_O^{\cdot\cdot}$—Ti'_{Ti} and $V_O^{\cdot\cdot}$—Ti'_{Ti}—$La_{Sr}^{\cdot}$ which localize free electrons and suppress their long-range migration. As a result, simultaneous enhancement of the dielectric permittivity and reduction of the dielectric loss were realized.



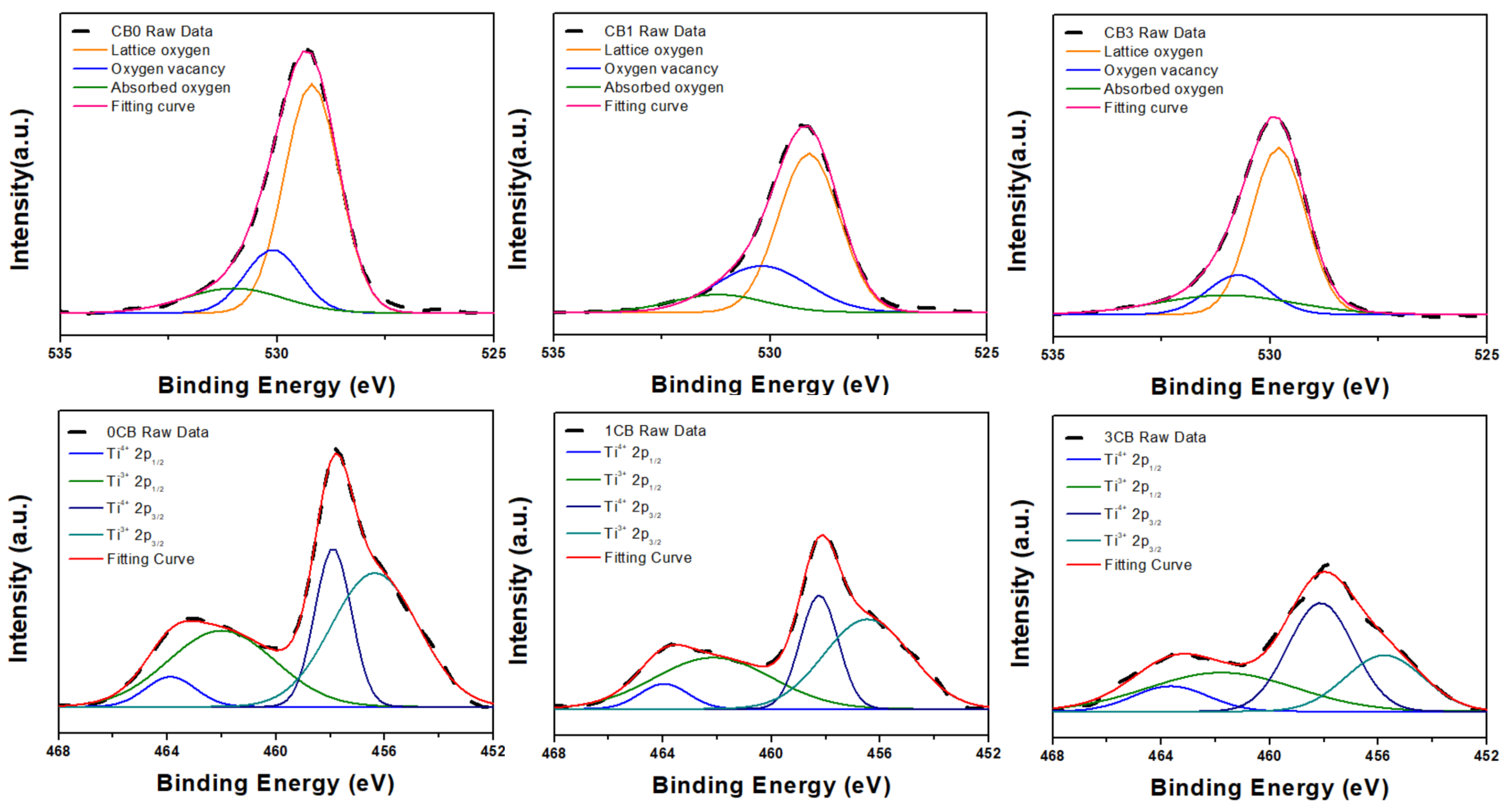


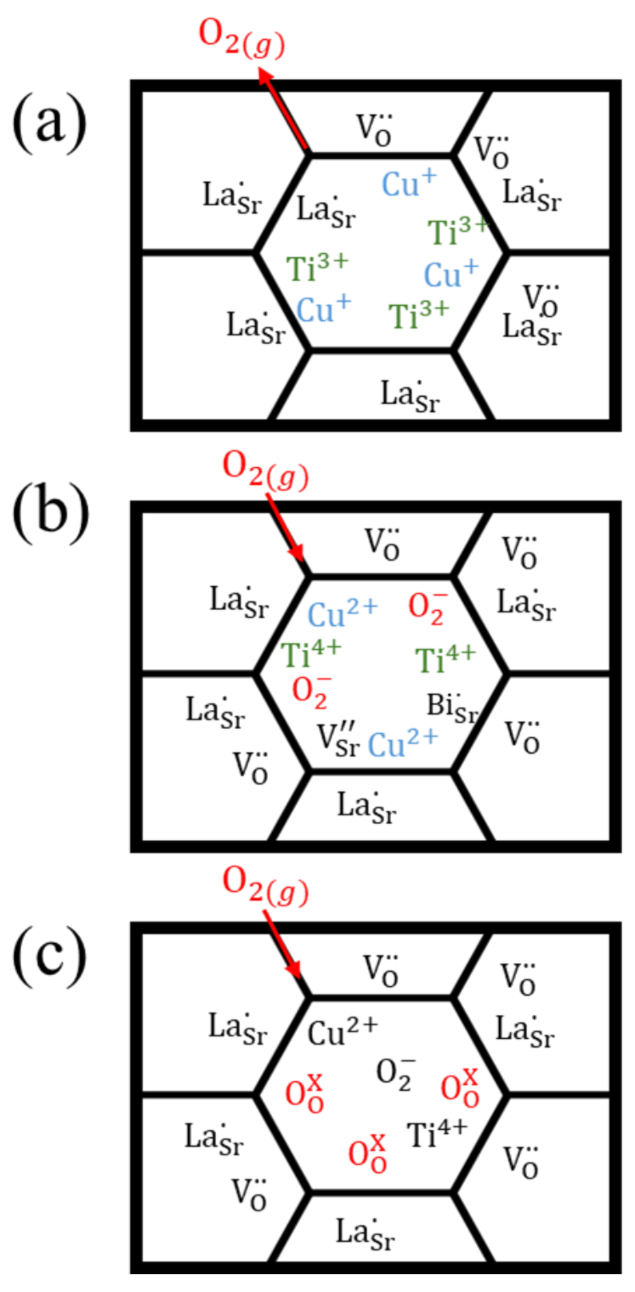
Experiment



- SrTiO3, TiO₂, La₂O₃ → Balling milling 24hr → Calcination 1100℃ 4hr (→ XRD) → Sintering under vaccum 1500℃ 3hr
- CuO, Bi₂O₃ → Balling milling 2hr → Sintering in air 750℃ 4hr (→ XRD) → Balling milling 2hr
- Adding TiO₂ and SiO₂ → Balling milling 24hr → Granulation+Pressing → Sintering in reducing atmosphere 1300℃ (→ Measure density) → Reoxidation in N₂ 900℃ 2hr → Paste Ag electrode → Electrical analysis

XPS





Reduction

$Cu^{2+} + e' \rightarrow Cu^{+}$

$Ti^{4+} + e' \rightarrow Ti^{3+}$

$O_O^X \rightarrow V_O^{\cdot\cdot} + \frac{1}{2}O_2 + 2e'$

Reoxidation

$Bi_2O_3 \xrightarrow{3SrO} 2Bi_{Sr}^{\cdot} + V_{Sr}'' + 3O_O^X$

$Cu^{+} \rightarrow Cu^{2+} + e'$

$Ti^{3+} \rightarrow Ti^{4+} + e'$

$O_2 + e' \rightarrow O_2^-$

Reoxidation

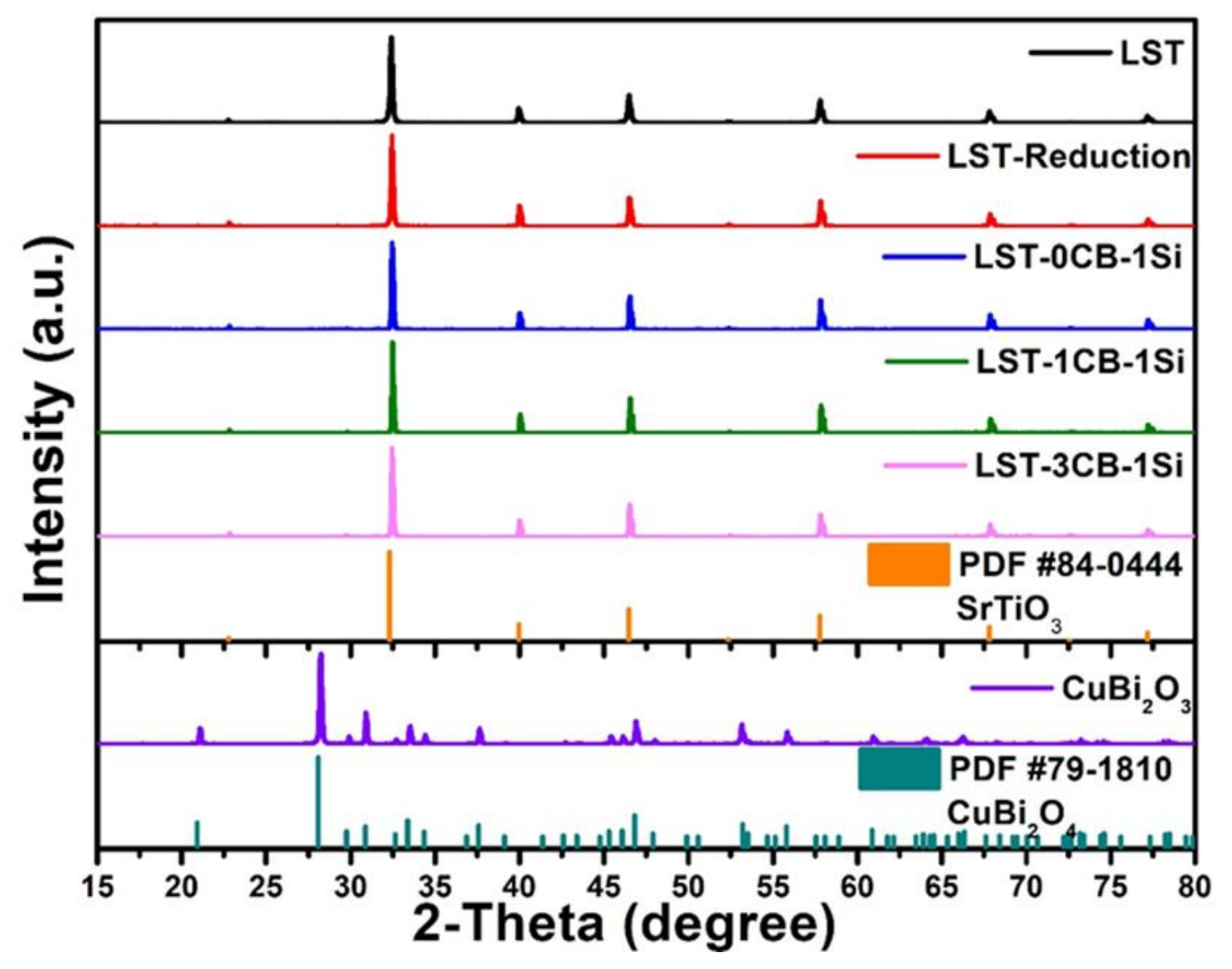
$V_O^{\cdot\cdot} + \frac{1}{2}O_2 + 2e' \rightarrow O_O^X$

$V_O^{\cdot\cdot} + O_2^- \rightarrow O_O^X$

Sample	Lattice oxygen		Oxygen vacancy		Absorbed oxygen	
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
0CB	529.2	70.6	530	23.6	531.6	5.8
1CB	529.1	71.3	530.2	20.8	531.2	7.9
3CB	529.8	74	530.7	17.5	531	8.5

Sample	2p 1/2				2p 3/2				Area ratio of Ti^{3+}
	Ti^{4+}		Ti^{3+}		Ti^{4+}		Ti^{3+}		
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)	
0CB	463.8	7.5	462	19.1	457.9	39.8	456.4	33.6	52.7
1CB	463.9	9	462.1	18.3	458.2	41.3	456.4	31.4	49.7
3CB	463.7	11	461.8	17	458.1	47.4	455.8	24.6	41.6

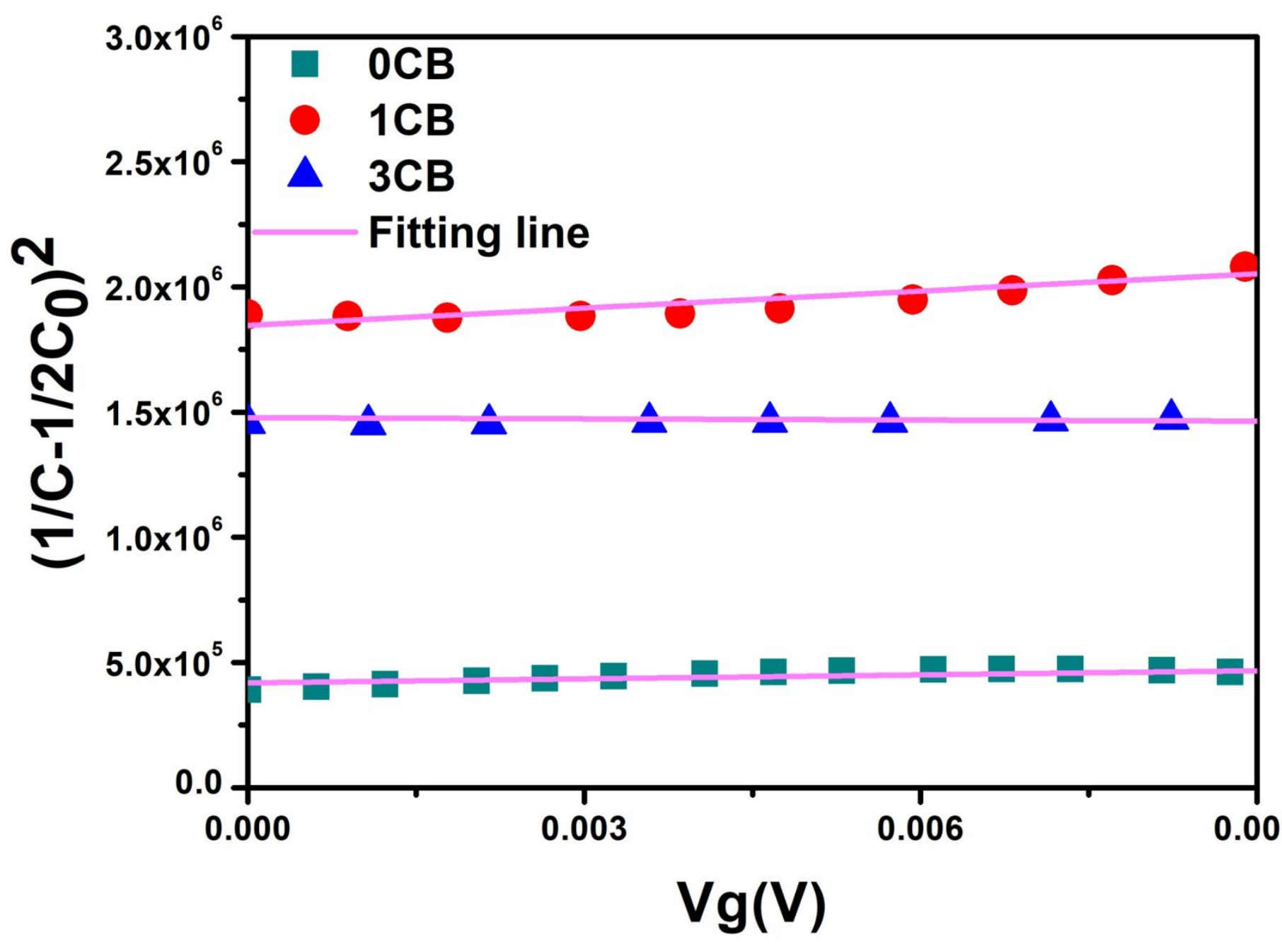
XRD



- All samples were all pure $SrTiO_3$ phase structure with no secondary phases.
- For LST and after reduction LST, lattice volume decreases indicates La³⁺ replace of Sr²⁺ and due to the generation of abundant oxygen vacancies in reduction .

Electrical Characterization

• Double Schottky Barrier



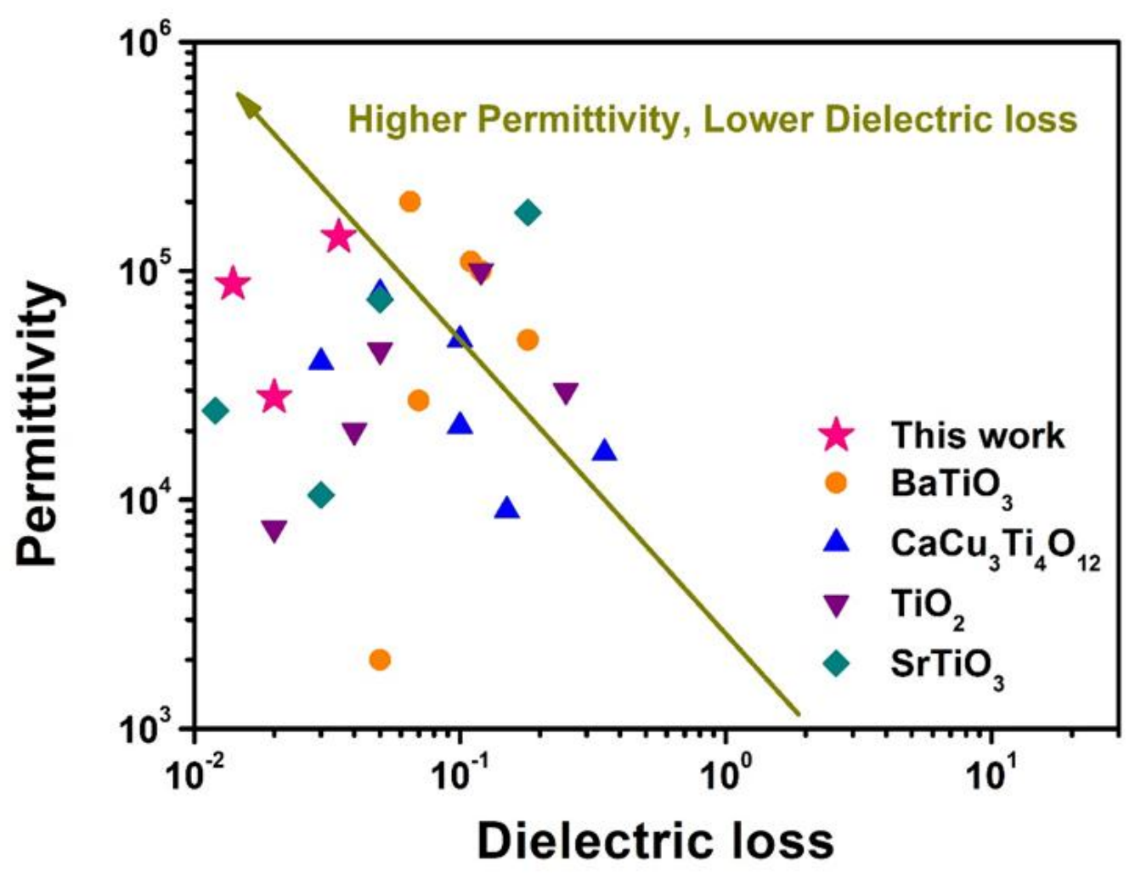
Donor: $La_{Sr}^{\cdot}$ 、$V_O^{\cdot\cdot}$ 、$Bi_{Sr}^{\cdot\cdot}$
Acceptor: O_2^- 、O_2^{2-} 、V_{Sr}'' 、Ti_{Ti}'

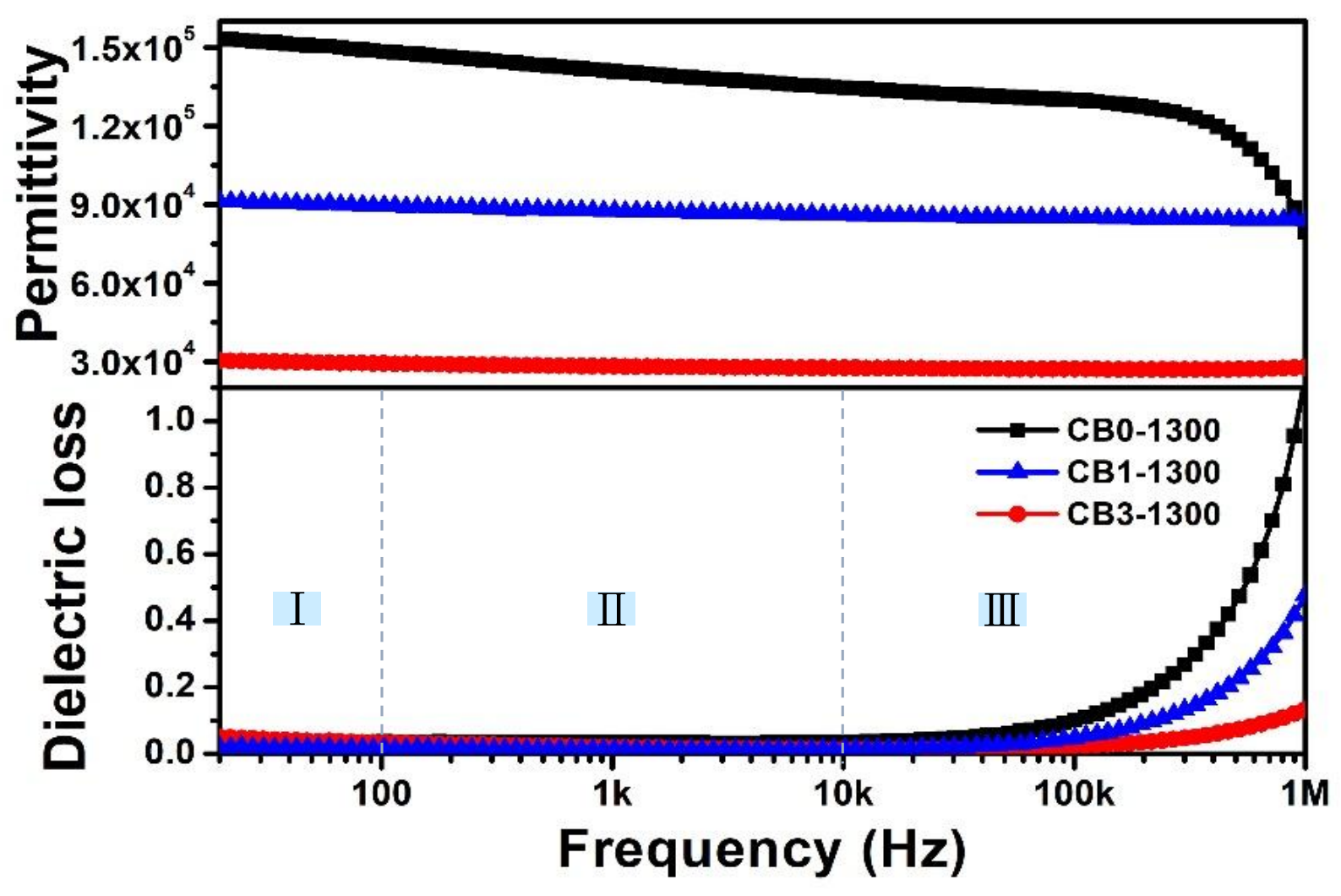
Sample	ϕ_b (eV)	N_d (m^{-3})	N_t (m^{-2})	W (nm)
0CB	0.03	1.96E+22	6.21E+14	31.7
1CB	0.08	2.35E+22	7.48E+14	31.8
3CB	0.30	1E+23	3.11E+15	30.9

Mott–Schottky analysis confirms that CB doping markedly increases the Schottky barrier height (ϕ_b), which strengthens grain-boundary insulation and suppresses space-charge polarization. As a result, dielectric loss (tan δ) is reduced, the dielectric constant remains stable, and the enhanced barrier structure critically improves varistor behavior with superior nonlinear electrical characteristics.

• Dielectric properties

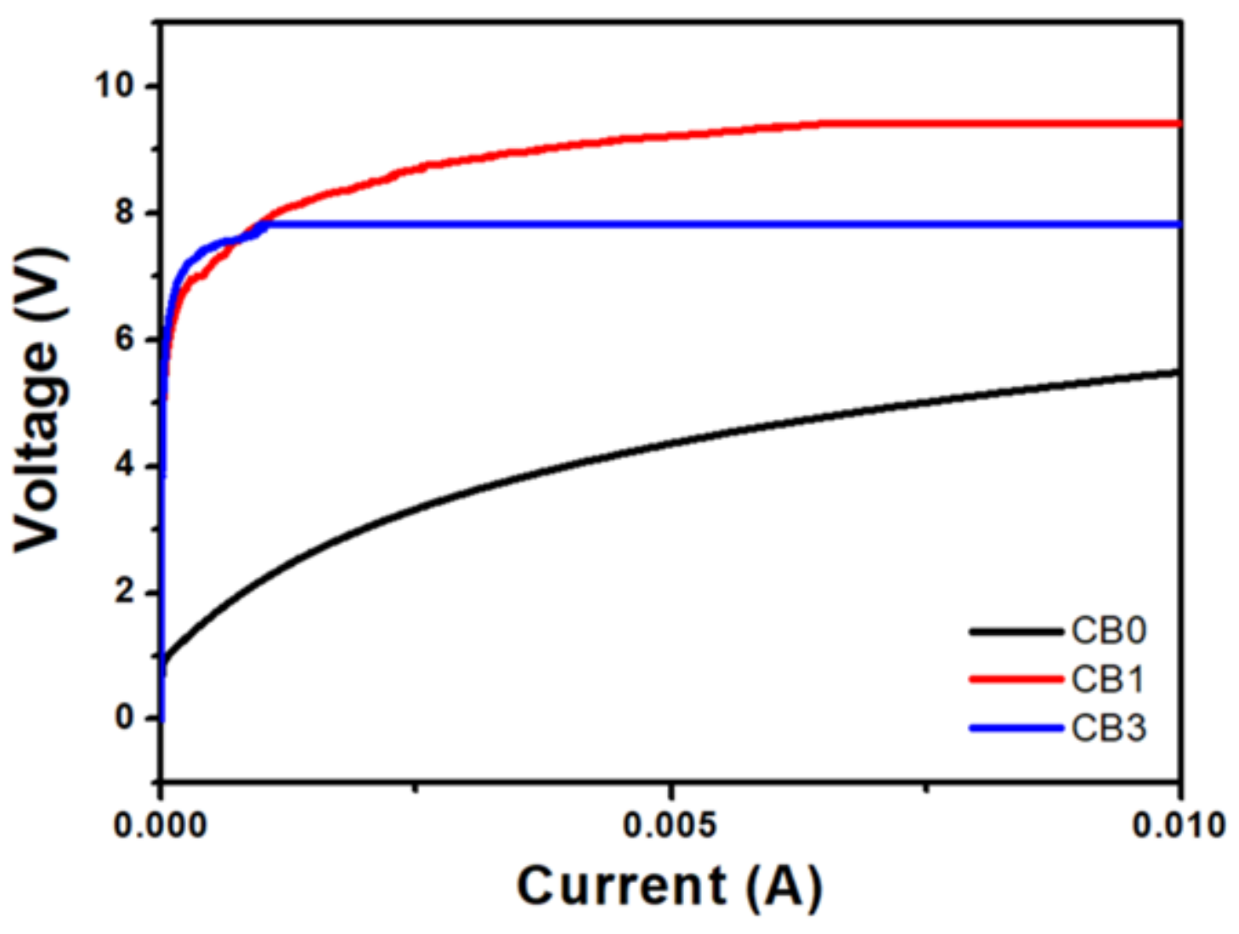
At low frequency, CuBi₂O₄ promotes oxygen diffusion and suppresses space charge polarization at the ceramic–electrode interface, reducing dielectric loss. At medium and high frequency, the increased Schottky barrier and EPDD effect restrict electron migration, maintaining a high dielectric constant and suppressing dielectric loss.





Sample		LST-xCB-Si		
CB amount (wt. %)		0	1	3
Relative Density (%)		89.73	91.39	92.55
E4990A	K	141000	87600	28100
	Tanδ	0.035	0.014	0.02

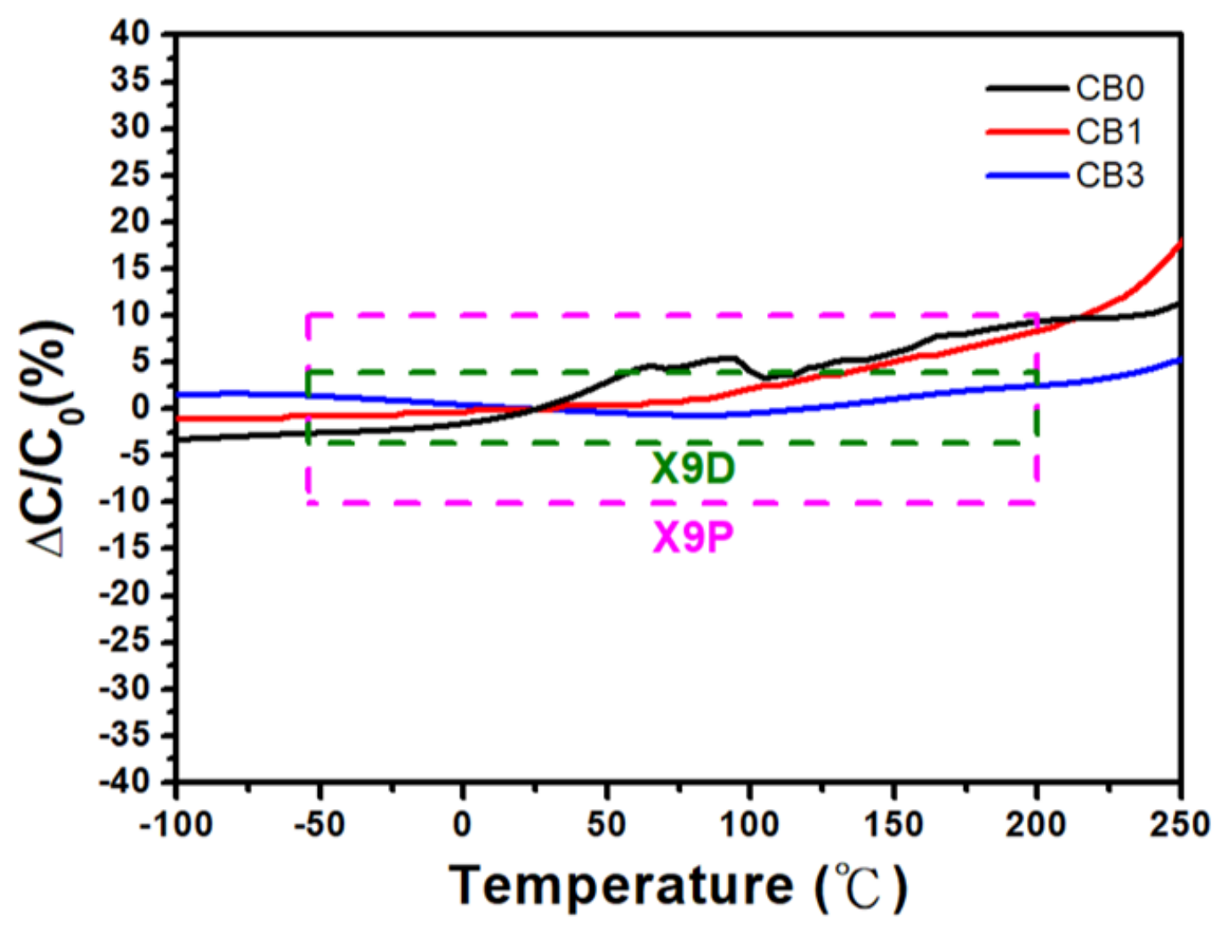
• Varistor properties



Cu²⁺ concentration at grain boundaries enhances the p-type doping effect. This strengthens the potential barrier height, thereby improving both the nonlinear coefficient (α) and breakdown voltage(V_b).

LST-CB_X-1Si	α	V_b(V /mm)	I_L(μA/cm²)
CB0	3.17	2.95	6.04E-04
CB1	9.64	10.1	1.13E-04
CB3	13.2	10.3	6.73E-05

• Temperature Coefficient of Capacitance



All samples demonstrate excellent temperature stability, satisfying the X9P capacitor temperature coefficient specification.

The ΔC/C₀ curves for CB1 and CB3 are notably flatter, with CB3 meeting the X9D specification, indicating significantly enhanced stability against temperature variations.

Conclusion

- Doping with CuBi₂O₄ lowers the sintering temperature to 1300 ˚C and promotes microstructural densification, demonstrating an excellent sintering-aid effect.
- CuBi₂O₄ doping suppresses space-charge polarization, reduces dielectric loss, and yields a stable dielectric frequency response. All samples satisfy the X9P specification, while CB3 further meets the X9D standard, demonstrating improved stability against both frequency and temperature variations.
- CuBi₂O₄ doping greatly enhances varistor characteristics, with higher nonlinear coefficient (α) and breakdown voltage (V_b) i, and reduced leakage current (I_L). This improvement stems from the n–p–n heterojunction formed at the LST/CuBi₂O₄ interface, which raises the Schottky barrier height at the grain boundaries.