

Effects of Bioderived Calcium Oxide Doping on the Microstructure and Phase Formation of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Superconductors

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ABSTRACT

A superconductor is a class of materials capable of conducting electrical current without resistance or energy loss when cooled below a specific critical temperature. However, high temperature superconductors such as $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (SmBCO) often suffer from weak link behavior at grain boundaries, which can negatively affect microstructural homogeneity and phase stability, limiting their practical performance. SmBCO is a well-known high temperature superconductor belonging to the $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ family, exhibiting zero electrical resistance at relatively higher temperatures compared to conventional superconductors. To overcome grain boundary limitations and improve its microstructure, this study investigates the incorporation of calcium oxide (CaO) extracted from natural cockle shells (*Cerastoderma edule*) into SmBCO using the solid-state reaction method, chosen for its simplicity, cost-effectiveness, and ability to yield materials with good phase purity and structural stability. SmBCO samples were synthesized with varying CaO weight percentages of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 wt.% to systematically examine the effect of CaO on grain connectivity, porosity, and phase formation. Comprehensive characterizations were performed using thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) to evaluate thermal stability, chemical bonding, crystalline structure, surface morphology, and elemental composition. Results indicate that CaO doping significantly enhances grain connectivity and reduces porosity, leading to improved microstructural homogeneity. XRD confirmed the formation of the primary SmBCO phase in all samples, with minor secondary phases appearing at higher CaO contents, suggesting an optimal doping threshold. Overall, the controlled addition of cockle shell-derived CaO provides an environmentally sustainable approach to improving the microstructural quality, phase stability, and performance of high-temperature SmBCO superconductors for advanced technological applications.

Keywords: SmBa₂Cu₃O_{7-δ} (SmBCO); calcium oxide; biogenic calcium oxide source; cockle shell

INTRODUCTION

SmBa₂Cu₃O_{7-δ} (SmBCO) is a high-temperature superconducting material belonging to the family of copper-oxide-based superconductors known as REBa₂Cu₃O_{7-δ} (REBCO) where RE denotes a rare-earth element [1]. Members of this REBCO family exhibit superconductivity above the boiling point of liquid nitrogen (77 K), which has fostered extensive research into their use in power transmission, magnetic levitation, and advanced electronics [2]. Studies of REBCO superconductors show that their relatively high critical temperatures and ability to support high critical currents make them promising for technological applications requiring efficient performance at cryogenic temperatures [3]. Like other cuprate superconductors, SmBCO displays type-II superconductivity, enabling it to maintain a superconducting state under high magnetic fields [4].

Dopant incorporation in high-temperature superconductors such as REBa₂Cu₃O_{7-δ} (REBCO) plays a crucial role in enhancing superconducting performance by modifying microstructure, grain boundary behavior, and flux pinning. In practical REBCO materials, weak links at grain boundaries limit inter-grain critical current density (J_c), and enhancing flux pinning remains a key focus to raise J_c under applied magnetic fields. Recent studies highlight that elemental doping or artificial pinning centers (APCs) introduces controlled defects that act as strong pinning sites, improving J_c and overall superconducting stability [5]. Elemental doping has been widely explored in coated conductors prepared by metal-organic deposition, where doped phases refine heterogeneous nanostructures and enhance flux pinning by providing effective vortex immobilization sites [6].

Artificial pinning center engineering through dopant incorporation has also been shown to dramatically increase J_c in REBCO superconductors. Self-assembled nanocolumnar inclusions, such as BaHfO₃ incorporated into REBCO films, have achieved record critical current densities and pinning forces, demonstrating that carefully engineered dopants can form highly effective flux pinning landscapes that sustain high current densities even under strong fields [7]. Broad reviews on flux pinning mechanisms confirm that elemental doping, second-phase embedding, and irradiation-induced defects are among the most effective methods to tailor superconducting properties by enhancing vortex immobilization and reducing anisotropy in critical current behavior [8].

These advances underscore that dopants serve multiple functions in REBCO systems: they refine microstructure, engineer grain boundary interfaces, and introduce artificial pinning centers that collectively improve phase stability, current-carrying capacity, and performance in technologically relevant conditions. While specific CaO doping studies on SmBCO are emerging, the general principles established in recent REBCO research provide a strong foundation for understanding how controlled dopant addition can improve microstructural quality and superconducting properties [5,9].

Calcium doping, while extensively studied historically in REBCO systems, remains a useful conceptual basis for understanding dopant effects on grain boundaries in these materials. Although specific recent Ca-doped SmBCO is sparse, research on closely related YBa₂Cu₃O_{7-δ} (YBCO) systems demonstrates that partial substitution of Ca²⁺ for Y³⁺ at grain boundaries increases local carrier density and enhances current

transport across misoriented grain boundaries by compensating charge depletion and improving hole concentration at the boundary region (e.g., enhanced carrier screening and local hole concentration at doped low-angle boundaries) [10]. Preferential Ca segregation at grain boundaries has been shown to expand dislocation cores and increase grain boundary critical current, suggesting that dopant-induced modification of electronic structure and defect fields can alleviate weak-link limitations in cuprate superconductors [11]. These mechanistic observations in YBCO support the expectation that appropriate levels of CaO doping could similarly reduce grain boundary resistance and improve intergrain connectivity in SmBCO, motivating its investigation in high-temperature superconductor research where direct evidence for the specific SmBCO system is still emerging.

This study aimed to investigate the effects of CaO doping on the microstructure and phase formation of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (SmBCO) superconductors. Calcium doping has been shown in related REBCO systems to improve grain boundary properties and enhance intergrain current transport, motivating its evaluation in SmBCO. These findings provide an initial understanding of the role of CaO in modifying the microstructure and phase stability of SmBCO superconductors and establish a foundation for future studies aimed at optimizing dopant levels to maximize superconducting performance.

MATERIALS AND METHODS

Synthesis of SmBCO

The cockle shells were cleaned to remove any organic matter and impurities. After cleaning, the shells were dried to eliminate any moisture content. The cockle shells were ground into a fine powder by using agate mortar and pestle for 1 to 2 hours calcined at 900 °C at heating rate of 2 °C/min and followed by cooling in air.

To synthesize SmBCO, a stoichiometric ratio of Sm_2O_3 , BaCO_3 , and CuO in the proportion of 1:2:3 was employed. Samarium(III) oxide (Sm_2O_3 , 99.99%), barium carbonate (BaCO_3 , 99.8%), and copper (II) oxide (CuO , 99.7%) were supplied by Alfa Aesar and used as received. The raw materials were precisely weighed and mixed. Subsequently, the bio-derived CaO at varying weight percentages ($x = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0 wt.%) were added into the SmBCO powders and thoroughly ground using an agate mortar and pestle for one hour. The resulting powder mixture was then placed into an alumina crucible and subjected to calcination in a high-temperature furnace at 900 °C, with a controlled heating rate of 2 °C/min and a cooling rate of 1 °C/min followed by air cooling. An intermediate grinding step was carried out for another hour using the same grinding method before the mixture was calcined again under identical conditions. After completing two calcination cycles, the resulting powder was compacted into pellets. These pellets were then sintered using a tube furnace, maintaining the same thermal parameters as the earlier calcination stage.

Samples Characterization

TGA

To evaluate thermal stability and decomposition characteristics, thermogravimetric analysis (TGA) was performed to track temperature-dependent weight variations in the sample. Thermal properties of the SmBCO powder were investigated using a Mettler

Toledo TGA/DSC instrument (Switzerland) between 30 °C and 900 °C. Approximately 20 mg of sample was precisely weighed, transferred to a platinum crucible, and heated at 10 °C/min under nitrogen gas flowing at 50 mL/min. The percentage mass loss was continuously monitored to establish the residual mass at specific temperature intervals.

XRD

X-ray diffraction (XRD) was conducted using a Rigaku Mini Flex II diffractometer (Japan) to determine the crystalline phases and crystallite sizes of CaO-added SmBCO samples. Approximately 0.3 g of each powder sample was uniformly spread onto an acetone-cleaned glass slide (0.2 mm depth) and scanned at 30 kV operating voltage across a 2θ range of 20°–80° at 2 °/min using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Crystalline phases were identified and crystallite sizes estimated through search-match database analysis of the resulting diffraction patterns.

SEM and EDX

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX, Tescan Vega) was employed to determine the elemental composition of SmBCO samples containing different CaO weight percentages. Sample preparation involved mounting SmBCO pellets on carbon tape-coated stubs, followed by gold sputter-coating for approximately 5 min to ensure adequate electrical conductivity and thermal stability. SEM observations were acquired at an accelerating voltage of 10 keV and beam current of 30 pA, while EDX spectra were collected from selected areas at 1000× magnification for quantitative elemental analysis.

RESULTS AND DISCUSSION

TGA of uncalcined SmBCO

The thermal decomposition profile of uncalcined pristine SmBCO powder from 30 °C to 900 °C is depicted in Figure 1. The weight loss stages correlate with optimal sintering conditions [12]. Initial minor weight loss below 100 °C corresponds to moisture evaporation and surface impurity removal. Stage 1 (250 °C – 375 °C) shows increased weight loss attributed to samarium oxide decomposition, while stage 2 (375 °C – 800 °C) displays the most significant mass reduction, characterized by a steep TGA decline and prominent DTG peak. The stoichiometric SmBCO phase (1:2:3 ratio of Sm:Ba:Cu) forms at 900 °C but degrades above this temperature due to oxygen loss and partial melting. TGA analysis suggests 900 °C – 920 °C as the ideal sintering range for maintaining phase stability and structural integrity in SmBCO.

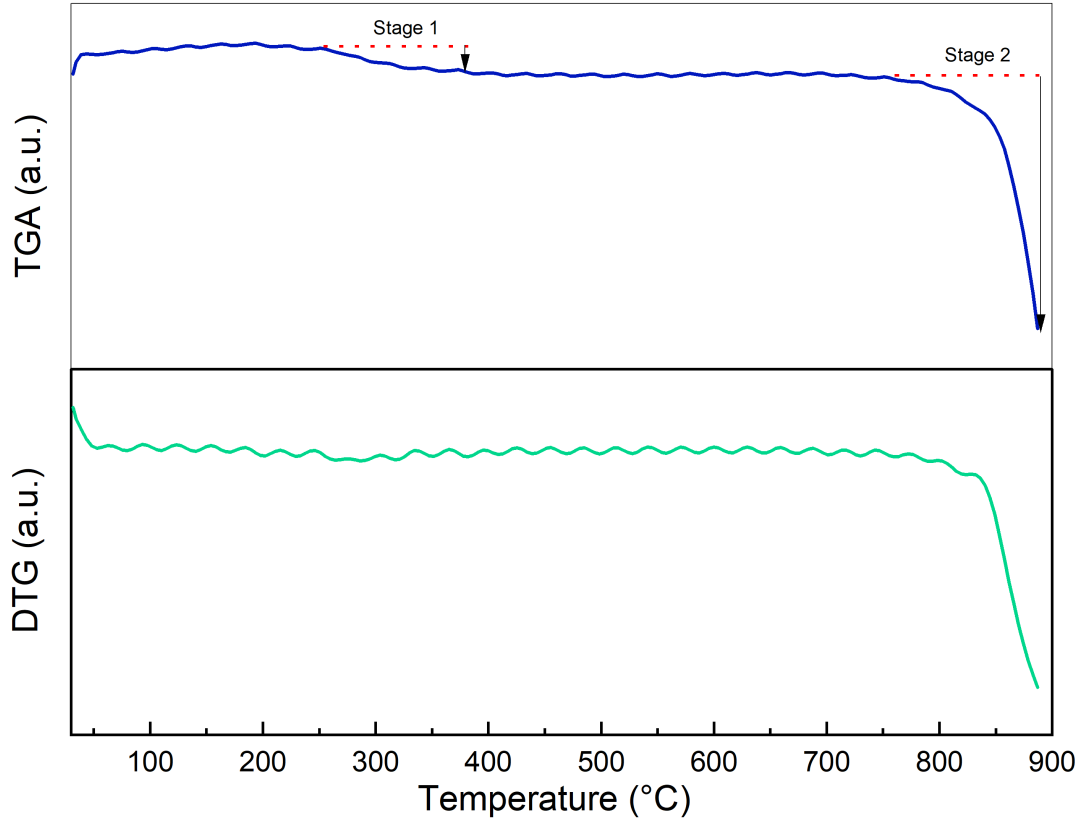


Figure 1. Thermogravimetric (TG/DTG) curves analysis of uncalcined pristine SmBCO powder

XRD analysis of SmBCO doped with bio-derived CaO

The crystalline structure and phase composition of bio-derived CaO-doped SmBCO samples were analyzed using Rigaku SmartLab software. Figure 2 presents the X-ray diffraction (XRD) patterns, revealing that all samples exhibited an orthorhombic crystal structure characteristic of the Sm-123 phase (PDF Card No. 00-039-1413), with minor CaO impurity peaks. The CaO phase was identified by a characteristic diffraction peak at $2\theta = 23.89^\circ$. Notably, a single dominant CaO peak was detected, with its intensity progressively increasing as a function of CaO concentration. Table 1 summarizes the lattice parameters (a , b and c) derived from XRD refinement, which showed slight variations with changing CaO content, confirming successful incorporation of CaO into the SmBCO lattice. The diminishing difference between the a and b parameters reflects a reduction in orthorhombicity. Enhanced orthorhombicity typically correlates with optimal oxygen stoichiometry, which is crucial for superior superconducting performance [13]. As illustrated in Figure 3, orthorhombicity decreased systematically with increasing CaO concentration, likely attributable to oxygen deficiency in the samples, which may compromise superconducting characteristics [14].

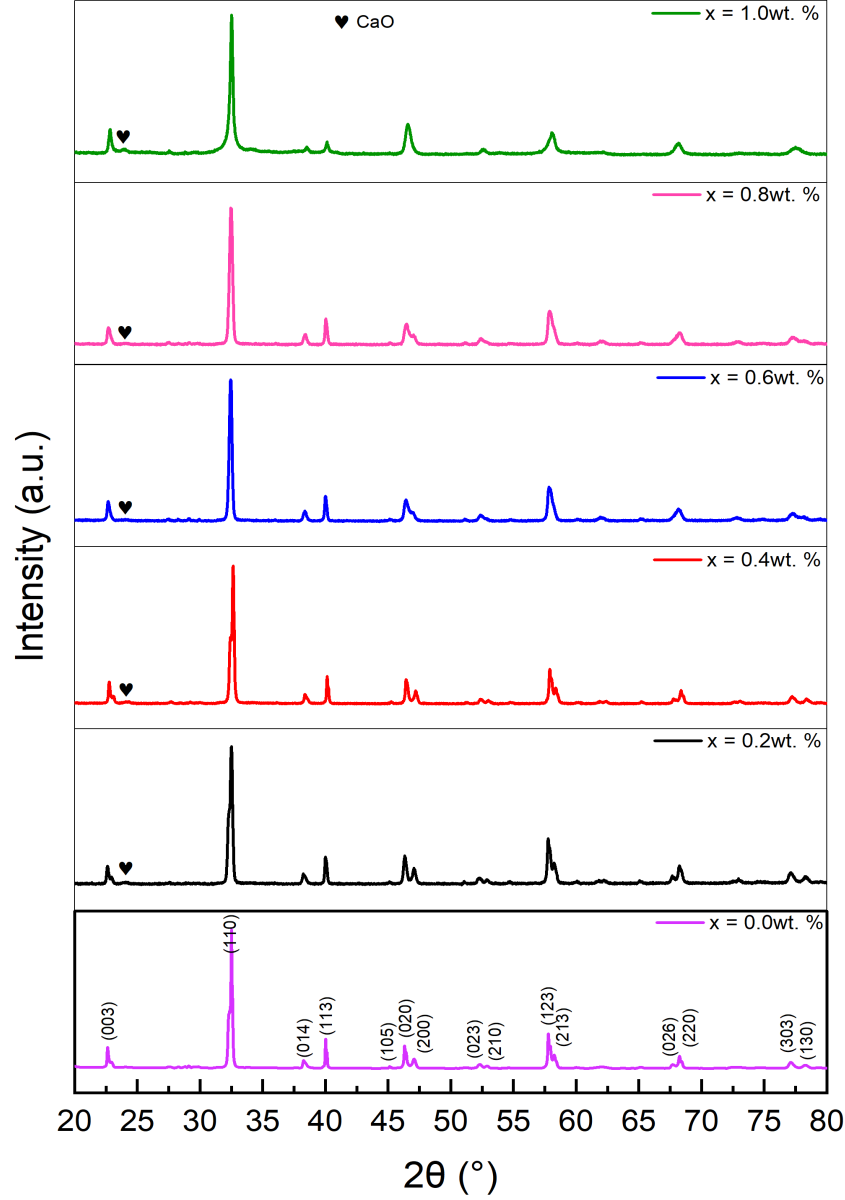


Figure 2. X-ray diffraction pattern of SmBCO with various additions of CaO

Table 1. Lattice constants a , b and c for CaO-doped SmBCO superconductor at different doping compositions, x

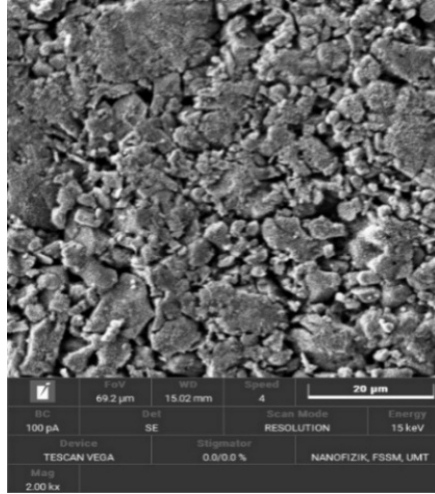
x	a (Å)	b (Å)	c (Å)	V (Å ³)	$\delta = [(b - a)/(b + a)]$
0.0	3.856	3.919	11.758	177.7	0.0081
0.2	3.856	3.919	11.758	177.7	0.0081
0.4	3.849	3.905	11.719	176.1	0.0072
0.6	3.879	3.916	11.765	178.7	0.0047
0.8	3.872	3.913	11.747	178.0	0.0053
1.0	3.849	3.905	11.719	176.1	0.0072

Microstructural and compositional analysis of bio-sourced CaO doped SmBCO using SEM-EDX

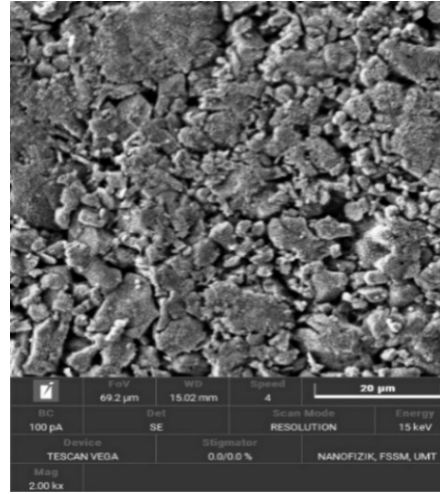
Figure 3 presents the surface morphology of cockle shell derived CaO doped SmBCO samples at 2000 $\times$ magnification. ImageJ software analysis of SEM images revealed a systematic trend in grain size variation across different CaO doping concentrations in the SmBCO superconductor. The average grain sizes for samples 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 wt.% are 4.711 μm , 4.888 μm , 5.714 μm , 6.245 μm , 6.562 μm and 7.170 μm , respectively. As the concentration of cockle shell-derived CaO increases, the average grain size increases, which can be attributed to enhanced grain growth during the solid state reaction process promoted by CaO addition [15]. Larger grain sizes in REBCO superconductors synthesized via the solid state reaction method are typically associated with reduced grain boundary density, leading to enhanced intergranular connectivity between particles [16]. This improved grain connectivity is particularly beneficial for superconducting performance, as calcium-containing additives have been demonstrated to enhance carrier density and current transport across grain boundaries in $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ materials [17].

The correlation between grain size and porosity reveals that as grain size increases with higher CaO content, the number of pores or voids tends to decrease due to improved grain connectivity and reduced porosity, which enhances the microhardness and resistance to fracture propagation among grains [18]. However, the sizes of individual pores exhibited an irregular trend throughout the doping range in this study, suggesting that while overall porosity decreases, the morphology and distribution of remaining pores may vary with CaO concentration.

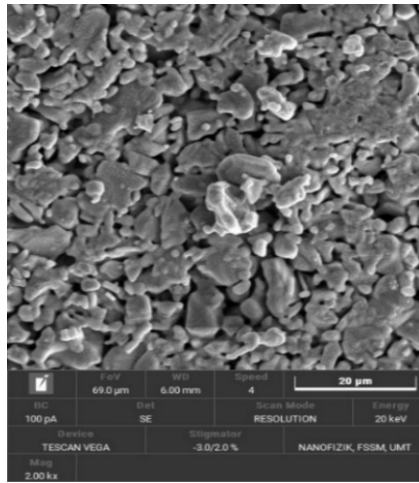
The EDX analysis presented in Table 2 demonstrates a systematic increase in calcium content with progressive CaO doping levels. Notably, copper concentration exhibits non-monotonic behavior, reaching a maximum at 0.6 wt.% CaO, suggesting that calcium incorporation may facilitate stabilization or redistribution of copper sites within the crystal structure. Oxygen stoichiometry displays a declining trend up to 0.6 wt.% CaO, followed by a subsequent increase at higher doping levels. This variation in oxygen content is particularly significant given its critical role in determining superconducting properties [13]. Samarium content shows an initial slight increase before declining at the highest CaO concentration (1.0 wt.%), potentially indicating partial substitution of samarium by calcium at elevated doping levels. Barium concentration remains relatively stable across all doping levels, indicating minimal displacement by calcium addition, consistent with findings reported by previous study [19]. Minor fluctuations in carbon content are observed, likely attributable to residual organic contaminants from sample preparation or processing conditions. The most uniform elemental distribution is achieved in samples containing 0.6 to 0.8 wt.% CaO, suggesting that this doping range represents the optimal composition for enhancing microstructural homogeneity and potentially improving the superconducting performance of SmBCO material.



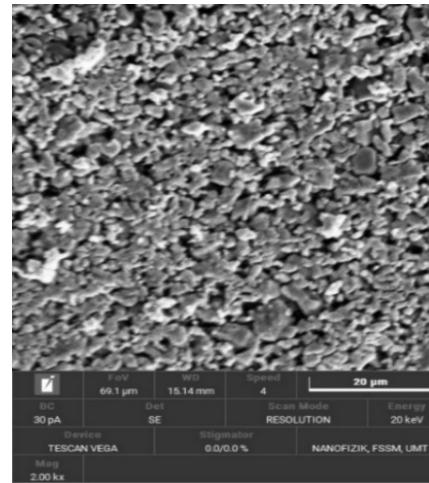
(a)



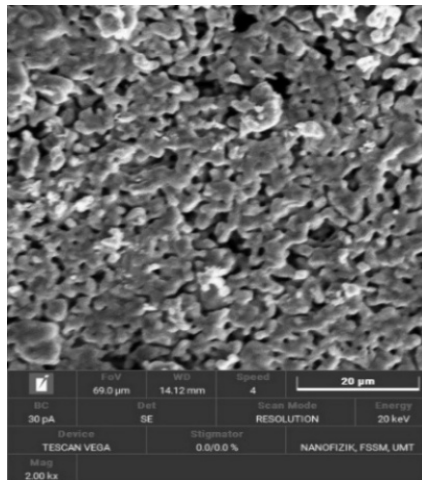
(b)



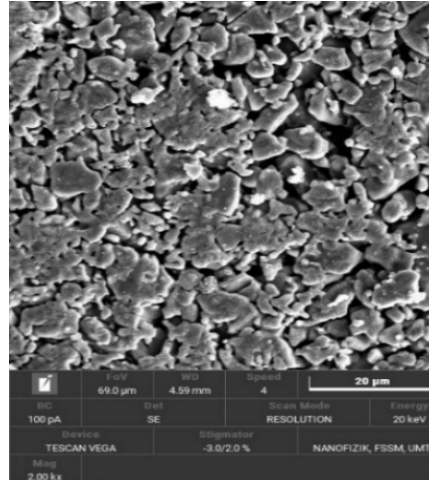
(c)



(d)



(e)



(f)

Figure 3. SEM micrographs of the surface of SmBCO doped with (a) 0.0 wt.%, (b) 0.2wt.%, (c) 0.4wt.% (d) 0.6wt.% (e) 0.8wt.% and (f) 1.0wt.% of CaO

Table 2 EDX elemental analysis of CaO doped SmBCO

SmBCO + <i>x</i> wt.% CaO	Elements (wt.%)								
	C	O	Cu	Ba	Sm	Ca	Na	Mg	Rb
0.0	15.33	47.76	18.10	12.95	5.85	0.00	0.00	0.00	0.00
0.2	10.69	43.09	21.53	15.12	6.91	0.17	2.03	0.28	0.17
0.4	15.40	38.32	3.08	13.10	6.09	3.08	2.62	1.49	0.89
0.6	17.63	32.76	22.29	15.95	7.40	0.85	2.30	0.44	0.37
0.8	14.67	36.72	21.21	14.96	6.88	0.84	2.98	1.35	0.39
1.0	18.77	42.02	17.93	12.55	5.51	1.20	1.76	0.08	0.17

CONCLUSIONS

This study successfully demonstrates that bio-derived calcium oxide from cockle shells effectively enhances the microstructural properties of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductors synthesized via solid-state reaction at $900^\circ\text{C} - 920^\circ\text{C}$. Systematic characterization through TGA, XRD, SEM, and EDX revealed that CaO doping progressively increased grain size from $4.711\ \mu\text{m}$ to $7.170\ \mu\text{m}$, improving grain connectivity and reducing porosity. The optimal doping range of $0.6 - 0.8\ \text{wt.}\%$ CaO exhibited the most uniform elemental distribution, balanced copper-oxygen stoichiometry, and superior microstructural homogeneity while maintaining the orthorhombic Sm-123 phase. However, reduced orthorhombicity at higher CaO concentrations indicates potential oxygen deficiency concerns. This research validates the use of sustainable, biogenic calcium sources for superconductor enhancement, offering both improved microstructural quality and environmental benefits through waste shell valorization. Future work should correlate these microstructural improvements with critical superconducting properties (T_c and J_c) to fully establish the functional advantages of bio-derived CaO doping in SmBCO for advanced technological applications.

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AUTHOR'S CONTRIBUTION STATEMENT

Conceptualization, A.R. and N.S.M.S.; Methodology, S.N.R.M.Y. and A.R.; Analysis and investigation, N.A.N. and N.M.M.H.; Validation, A.R. and M.M.A.K.; Data curation, A.R. and M.M.A.K.; Writing – Original Draft Preparation, A.R.; Writing – Review & Editing, A.R.; Visualization, A.R. and S.N.R.M.Y.; Supervision, A.R. and N.S.M.S.; Project Administration, A.R.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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