Solid State Science and Technology, Vol. 33, No. 2 (2025) 119-126
https://doi.org/10.66514/ssst33-2-119-126

Effect of La_2O_3 Doping on the Hardness, Microstructure and Void Formation of Sn-Ag-Cu (SAC305) Lead-Free Solder Alloys

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(Received: 4 December 2025 / Revised: 27 December 2025 / Accepted:30 December 2025 / Published online: 31 December 2025)

ABSTRACT

The transition to lead-free solders in response to environmental regulations has established Sn-Ag-Cu (SAC) alloys as the industry standards. However, their reliability is limited by coarse microstructures, excessive intermetallic compound (IMC) growth, and susceptibility to void formation. This study investigates the microalloying of SAC305 solder with lanthanum oxide (La_2O_3) to enhance micromechanical properties and refine microstructure. SAC305 pastes doped with 0.5–5.0 wt.% La_2O_3 were prepared, reflowed on copper substrates, and characterized. Nanoindentation tests revealed substantial improvements in hardness and elastic modulus, with the most pronounced enhancement at 1.5 wt.% La_2O_3, where hardness and modulus increased by approximately 2408.76% and 1767.25%, respectively, compared to the undoped alloy. Microstructural analysis confirmed that La_2O_3 acts as a potent grain refiner, promoting heterogeneous nucleation for finer β-Sn grains and stabilizing IMC phases such as Cu_6Sn_5 and Ag_3Sn. Additionally, La_2O_3 doping suppressed void formation by improving wetting and facilitating gas escape during solidification. These findings demonstrate that La_2O_3 is an effective reinforcement for SAC solder, enabling superior mechanical performance through microstructural control and void reduction. These results are useful in advancing the development of high-reliability lead-free solder systems for demanding applications in electronic packaging, where joint integrity under thermal and mechanical stress is critical.

Keywords: Lanthanum oxide; lead-free solder; microalloying; nanoindentation; reliability

INTRODUCTION

The rapid advancement and miniaturization of electronic devices have intensified the demand for reliable interconnection technologies, where solder joints serve as critical components for both electrical continuity and mechanical stability. These joints endure significant stresses from thermal cycling, vibration, and mechanical loading, making their durability a decisive factor in overall system performance [1,2]. As electronic assemblies become more compact and operate under harsher conditions, the need for solders with superior mechanical strength and thermal reliability has grown substantially.

Historically, Sn-Pb eutectic solders dominated electronic packaging due to their favorable melting characteristics and ductility. However, environmental and health regulations restricting lead usage have driven the industry toward lead-free alternatives. Among these, Sn-Ag-Cu (SAC) alloys—particularly Sn-3.0Ag-0.5Cu (SAC305)—have emerged as the most widely adopted due to their excellent thermal fatigue resistance and mechanical properties[1,3]. Despite these advantages, SAC solders still exhibit limitations such as coarse microstructures, excessive intermetallic compound (IMC) growth, and susceptibility to void formation, which collectively compromise joint reliability under cyclic loading and high-temperature conditions [4–8].

To address these challenges, alloy modification through microalloying has gained attention, with rare-earth (RE) elements offering promising solutions. RE additions such as cerium (Ce), lanthanum (La), and holmium (Ho) have demonstrated the ability to refine β-Sn grains, suppress IMC coarsening, and enhance mechanical uniformity [9–11]. Furthermore, incorporating RE oxides into SAC solders has shown potential for improving hardness, creep resistance, and interfacial adhesion, thereby mitigating brittle fracture risks [12–14]. These improvements are particularly relevant for high-reliability applications in aerospace and defense electronics, where solder joints must withstand extreme thermal and mechanical stresses.

The present study focuses on the effect of lanthanum oxide (La_2O_3) doping on SAC305 solder, specifically examining its influence on hardness, microstructural refinement, and void formation. By exploring the role of La_2O_3 in modifying IMC morphology and enhancing micromechanical properties, this research aims to contribute to the development of environmentally sustainable, high-performance solder systems aligned with global initiatives such as SDG 12 for responsible production. Understanding these effects is essential for improving solder joint reliability and extending the operational lifespan of advanced electronic assemblies.

MATERIALS AND METHODS

The experimental work began with the preparation of SAC305 solder alloy as the base material. High purity La_2O_3 powder (99.9% purity, median particle size D_{50} = 17.0 μm) was incorporated into the SAC305 matrix at concentrations of 0.5, 1.0, 1.5, and 2.0 wt.%, along with an undoped control sample (Table 1). These compositions were selected to evaluate the effect of La_2O_3 on microstructural evolution and mechanical properties. For each composition, 50 g of solder paste was homogenized using mechanical stirring at low speed for 5 min to ensure uniform nanoparticle dispersion and minimize agglomeration. The solder paste was stored at 5 °C to maintain flux stability, equilibrated to room temperature before mixing, and then applied onto copper-finished PCBs using a stainless-steel stencil for consistent thickness.

Table 1. Composition of SAC305 and La_2O_3-doped samples

Composition	Label	SAC (wt.%)	La_2O_3 (wt.%)	Total (wt.%)
SAC305	Control	100.0	0.0	100
SAC305 + 0.5La	SAC+LaO1	99.5	0.5	100
SAC305 + 1.0La	SAC+LaO2	99.0	1.0	100
SAC305 + 1.5La	SAC+LaO3	98.5	1.5	100
SAC305 + 2.0La	SAC+LaO4	98.0	2.0	100

Soldering process was performed in a TYR108N-C lead-free reflow oven following a four-stage thermal profile: preheating (up to 150 °C), soaking (185 °C for 1 min), reflow (peak at 225 °C for 8 min), and controlled cooling to 30 °C. This profile replicated industrial SMT conditions while minimizing defects such as voids and irregular IMC growth.

For microstructural analysis, samples were sectioned to 5 × 7 × 1 mm^3 dimensions using a precision saw, cleaned, and mounted in cold-curing epoxy. Grinding employed SiC papers from P180 to P4000 under water cooling, followed by polishing with diamond suspensions (1 μm and 0.25 μm) to achieve a mirror finish. Etching in 5% HCl–methanol revealed IMC layers for microscopic observation.

Nanoindentation tests were conducted using a TI-950 Triboindenter with a Berkovich tip under ISO 14577 standards. Indentations were performed at maximum load of 10 mN load with controlled rates of 0.5 mN/s and 30 s holding times to minimize creep. Hardness and modulus values were derived using the Oliver–Pharr method.

RESULTS AND DISCUSSION

Hardness and Reduced Modulus

The effect of lanthanum oxide (La_2O_3) doping on the hardness and reduced modulus of SAC solder alloys was investigated, and the results are summarized in Table 2 and illustrated in Figures 1 and 2. The base SAC alloy exhibited no change in hardness or modulus, serving as the reference. Upon doping with La_2O_3, a significant improvement in both properties was observed.

Table 2. The micromechanical properties of SAC305 and La_2O_3 doped SAC305 solder

Sample	Hardness Percent Change	Reduce modulus Percent Change
SAC	-	-
SAC+LaO1	88.05	249.37
SAC+LaO2	394.82	421.09
SAC+LaO3	2408.76	1767.25
SAC+LaO4	2004.38	1530.26

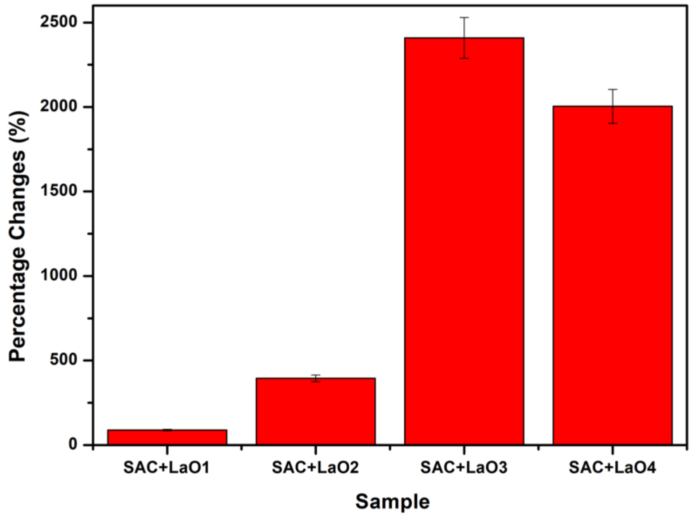


Figure 1. Percent change in hardness with La_2O_3 content

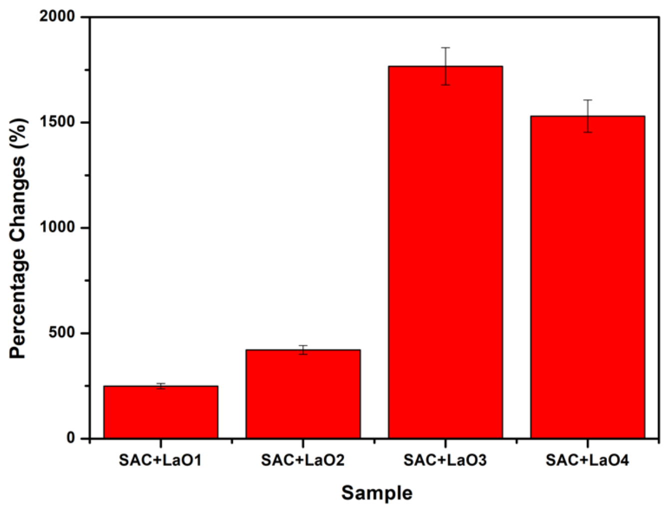


Figure 2. Percent change in reduced modulus with La_2O_3 content

Hardness

The hardness of SAC solder increased dramatically with La_2O_3 addition. At the lowest doping level (SAC+LaO1), hardness improved by 88.05%, while SAC+LaO2 showed a 394.82% increase. The most notable enhancement occurred at SAC+LaO3, where hardness surged by 2408.76%, followed by SAC+LaO4 at 2004.38%. This trend suggests that La_2O_3 acts as a potent reinforcement agent, likely due to grain refinement and the formation of intermetallic compounds (IMCs) that impede dislocation motion. Similar findings were reported that rare-earth doping improved mechanical strength through microstructural modification [10,13,15].

Reduced Modulus

A parallel trend was observed for reduced modulus, which reflects the elastic stiffness of the solder. SAC+LaO1 exhibited a 249.37% increase, SAC+LaO2 reached 421.09%, while SAC+LaO3 and SAC+LaO4 achieved 1767.25% and 1530.26%, respectively. The sharp rise at higher doping levels indicates enhanced rigidity, which can be attributed to the uniform distribution of La_2O_3 particles and their interaction with Sn-rich phases, as discussed by [16–18].

Microstructure and Void Formation

The improvement in hardness and reduced modulus is closely linked to microstructural refinement. The addition of La_2O_3 promotes heterogeneous nucleation, resulting in finer β-Sn grains and more uniform intermetallic compounds (IMCs) such as Cu_6Sn_5 and Ag_3Sn. This refinement helps reduce void formation during solidification and thermal cycling because smaller grains and well-dispersed oxides minimize shrinkage porosity. Previous studies [7,19] have shown that void formation in SAC solders is often associated with coarse microstructures and uneven IMC distribution; therefore, La_2O_3 doping mitigates these issues by stabilizing the microstructure.

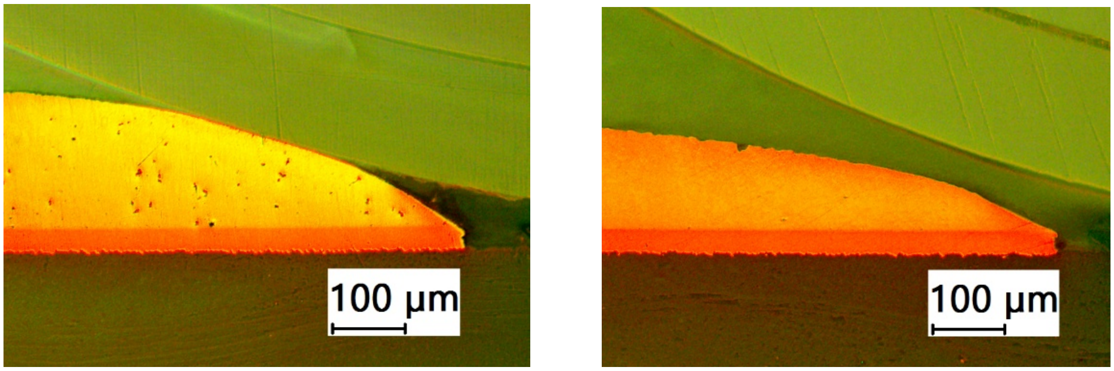
The peak improvement at SAC+LaO3 for both hardness and reduced modulus (Figures 1 and 2) indicates an optimal doping level, beyond which improvement levels off or slightly decreases (as seen in SAC+LaO_4). Excessive La_2O_3 may cause particle agglomeration, creating stress concentration sites that offset the benefits of grain refinement, consistent with findings reported by [20].

Figure 3(a) shows the microstructure of the control SAC solder joint without La_2O_3 doping, while Figure 3(b) represents the SAC solder doped with La_2O_3. A clear difference in void formation is observed between the two samples. The control sample exhibits a high density of microvoids distributed throughout the solder bulk, including several large voids near the interface region. In contrast, the La_2O_3-doped sample demonstrates a significantly reduced number of voids, with only a few small voids visible and no large void clusters.

The reduction in void formation can be attributed to the role of La_2O_3 as a grain refiner and oxygen scavenger. Lanthanum oxide tends to react with residual oxygen during the reflow process, reducing oxide film formation on solder surfaces and improving wetting behavior. This enhanced wetting minimizes entrapment of flux residues and gases, which are primary contributors to void nucleation during solidification [8,19,21]. Furthermore, La_2O_3 addition promotes heterogeneous nucleation, leading to finer and more uniform microstructure. A refined microstructure facilitates better diffusion paths for gas escape during soldering, thereby reducing void density [7,19].

Void formation in solder joints is a critical reliability concern because voids act as stress concentrators, reducing mechanical strength and accelerating crack propagation under thermal cycling or mechanical loading [2,19]. The observed improvement in void suppression with La_2O_3 doping suggests enhanced joint integrity and reliability, which correlates with reported improvements in hardness and creep resistance in rare-earth-doped SAC solders [14,22,23].

Overall, the microstructural evidence indicates that La_2O_3 doping improves solder joint quality by reducing void formation and refining grain structure. These changes are strongly correlated with enhanced mechanical properties such as hardness, creep resistance, and fatigue life, as supported by previous studies. Therefore, La_2O_3 doping represents a viable strategy for improving solder joint reliability in high-performance electronic packaging.



(a) (b)

Figure 3. The cross section of (a) SAC solder and (b) SAC + LaO3

CONCLUSIONS

La_2O_3 doping markedly improves the mechanical integrity of SAC305 solder alloys, as evidenced by significant increases in hardness and elastic modulus. The most pronounced enhancement occurs at 5 wt.% La_2O_3, where hardness increases by approximately 2408.76% and elastic modulus by 1767.25% compared to the undoped alloy. These improvements are directly linked to microstructural evolution: La_2O_3 facilitates heterogeneous nucleation, producing refined β-Sn grains and stabilizing intermetallic phases such as Cu_6Sn_5 and Ag_3Sn. This refined microstructure strengthens the solder matrix and impedes dislocation motion, thereby translating microstructural control into superior mechanical performance. The findings highlight La_2O_3 as an effective dopant for tailoring solder alloy properties through controlled grain and phase architecture, offering practical benefits for improving reliability in electronic packaging.

ACKNOWLEDGEMENTS

This research is fully supported by Fundamental Research Grant Scheme, FRGS/1/2023/STG05/UPNM/02/01. The authors fully acknowledged Ministry of Higher Education (MOHE) and National Defence University of Malaysia for the approved fund which makes this important research viable and effective. The authors also appreciated Universiti Kebangsaan Malaysia, RedRing Solder (M) Sdn. Bhd and Lynas Malaysia Sdn. Bhd. for sharing research materials and collaboration work.

AUTHORS' CONTRIBUTIONS STATEMENT

Conceptualization, W.Y.W.Y. and M.M.M.H.; Methodology, M.M.M.H. and A.Y.; Analysis and Investigation, M.M.M.H. and A.H.A.Y.; Validation, W.Y.W.Y., A.A., N.A., and N.A.A.M; Data curation, M.M.M.H. and W.Y.W.Y.; Writing—Original Draft Preparation, M.M.M.H. and A.H.A.Y.; Writing—Review and Editing, A.A., N.A. and W.Y.W.Y.; Visualization, M.M.M.H.; Supervision, W.Y.W.Y. and A.A.; Project Administration, W.Y.W.Y.

CONFLICT OF INTEREST

All authors declare no conflict of interest.

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