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Grain growth in $CaMnO_3$ ceramics under multimode microwave sintering

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Introduction

Global issues such as environmental pollution, climate change, and the energy crise has intensified the need for sustainable materials for clean energy conversion and storage [1].

Microwave-assisted sintering has gained attention as an energy-efficient alternative to traditional methods, offering advantages such as faster heating rates, limited grain growth, and energy savings of up to 80% [2,3]. This technique is particularly effective for materials with high dielectric or magnetic losses, or significant electrical conductivity, enabling rapid volumetric heating and improved mass transport [2,4–6].

However, despite these benefits, the interaction between microwave radiation and ceramic materials remains insufficiently understood, especially regarding its influence on structural and microstructural characteristics [6–8].

Among the promising materials, calcium manganite ($CaMnO_3$ or CMO) stands out due to its n-type semiconducting behavior, high Seebeck coefficient (~350 μV/K), and low thermal conductivity (~3 W/mK). Its adaptable perovskite crystal structure supports extensive cation doping, which can further enhance its thermoelectric properties [9].

This work aims to examines the impact of microwave sintering on the densification, structure, and microstructure of CMO ceramics, aiming to refine processing parameters for energy-related applications.

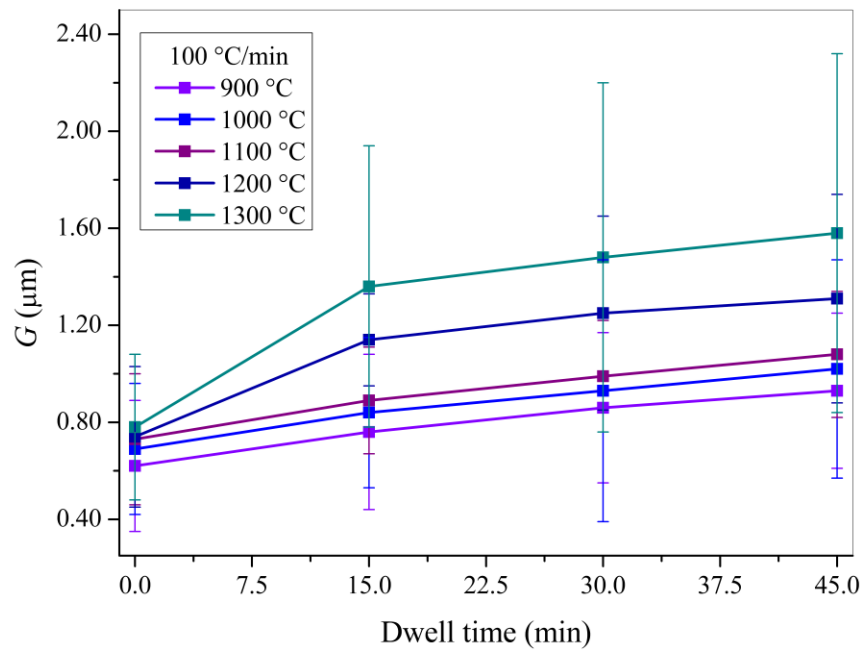


Figure 2. Grain size as a function of temperature and dwell time.

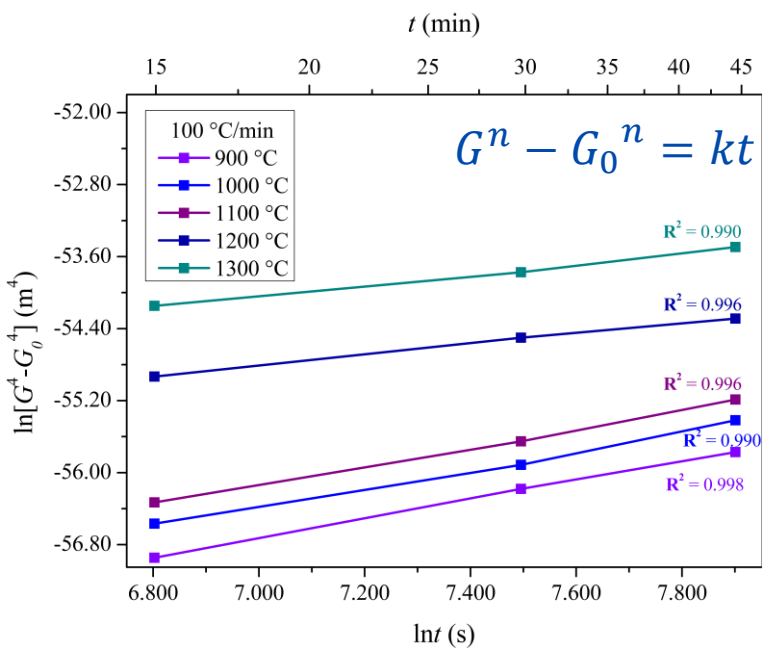


Figure 3. Grain growth exponent for CMO ceramics.

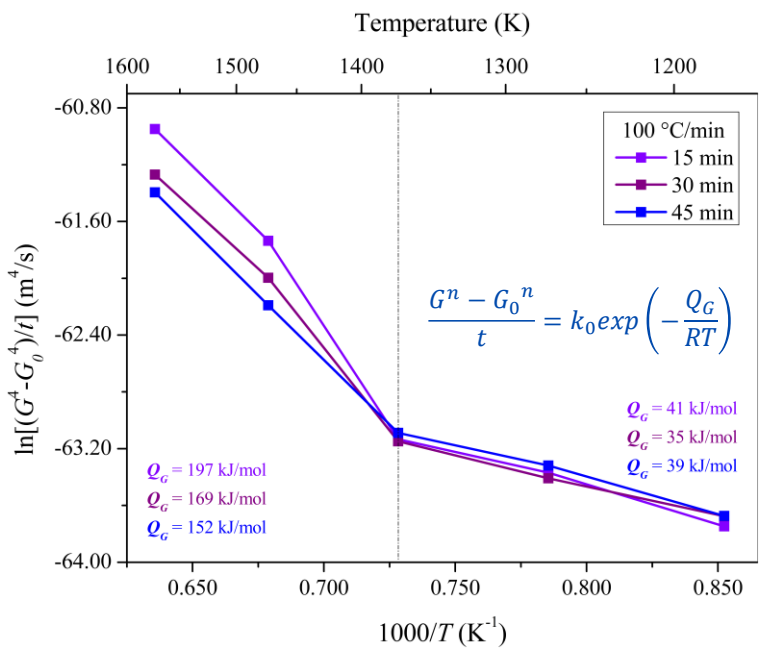


Figure 4. Activation energy for grain growth exponent for CMO ceramics.

Methodology

Solid state reaction
- **Raw precursors:** $CaCO_3$ and MnO
- **Mixture:** ball mill
  - ✓ Time: 3h30
  - ✓ Velocity: 144 rpm

Calcination
- **Temperature:** 1000 °C
- **Dwell time:** 3 h
- **Heating rate:** 10 °C/min
- **Atmosphere:** air

Characterization of the calcined powders
- **Structural:** XRD
- **Morphology/Particle size:** SEM
- **Chemical microanalysis:** EDS

Uniaxial pressing of the pellets
- **Pressure:** 175 MPa
- **Shape:** pellets:
  - ✓ **Diameter:** ~12.00 mm
  - ✓ **Thickness:** ~2.00 mm

Microwave sintering
- **Frequency:** 2.45 GHz
- **Temperatures:** 900–1300 °C
- **Dwell times:** 0, 15, 30 and 45 min
- **Heating rates:** 100 °C/min

Characterization of the calcined powders
- **Microstructural:** SEM
- **Chemical microanalysis:** EDS

Determination of grain growth kinetics
- Identification of grain growth mechanisms (n)
- Activation energy for grain growth (Q_G)

Results

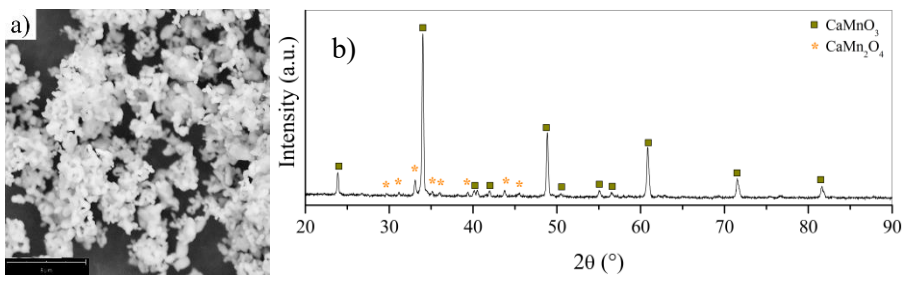


Figure 1. a) SEM and b) XRD of the CMO-based powder.

Conclusions

The grain growth behavior followed a kinetic exponent of n = 4, suggesting a mechanism governed by grain boundary diffusion associated with second-phase coalescence. Based on this mechanism, the activation energy for grain growth (Q_G) at higher temperatures was estimated to be around 170 kJ/mol.

References

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National Council for Scientific and Technological Development of Brazil (CNPq – Grant Nº. 316730/2023-8 and INCT 406322/2022-8), Minas Gerais State Foundation of Support to the Research (FAPEMIG – Grant Nº. APQ-01856-22) and Coordination for the Improvement of Higher Level or Education-Personnel (CAPES – Grant Nº 23038.003930/2024-79).