



Relationship between densification behavior and stabilization of quasi-liquid grain boundary layers in CuO-doped $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ microwave ceramics



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ABSTRACT

In a combination with aberration-corrected TEM and water quench treatment, $\text{CuO-xCu}_2\text{O}$ grain boundary quasi-liquid layers in multicomponent $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ perovskite microwave ceramics doped by 0.5 wt% CuO are observed. Their structure and chemistry are identified. The relationship between their stabilization and densification behavior during the early sintering stage is clarified by constant-heating-rate/isothermal sintering experiments. It is revealed that the densification of CuO-doped $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ ceramics is dominated by viscous flow mechanism. Additionally, the appearance of quasi-liquid layers during the early sintering stage promotes mass transport by short-circuit diffusion. These results can be used as a guide to control the microstructure and properties of microwave ceramics.

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Significant progress of wireless communication techniques provide a powerful impetus to explore dielectric materials in the past decades, including commercial $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ (CTNA) microwave ceramics [1–3]. It is well recognized that intrinsic dielectric loss of these complex multicomponent perovskites is very low. In contrast, extrinsic factors, including porosity, grain size, grain boundary, impurities, secondary phases, and point defects, can play a dominant role in determining measured quality factor ($Q \times f$) values [4–9]. However, elevated sintering temperature and long sintering time can result in nonstoichiometry of ceramics and induce point defects into perovskite, which can significantly degrade the microwave properties [10–16].

Several strategies can be used to reduce the sintering temperature and enhance the densification of ceramics. The common and practical one is to dope low melting point oxides as sintering aids, such as B_2O_3 [17], CuO [18], Li_2CO_3 [19], and $\text{BaCu}(\text{B}_2\text{O}_5)$ [20] et al. A series of studies revealed that the stabilization of disordered or quasi-liquid interfacial films well below bulk eutectic temperature is related to solid-state activated sintering mechanism in inorganic materials. However, there are few reports concerning the sintering behavior and densification mechanism of complex multicomponent perovskite microwave ceramics. Especially, CuO has been

widely used in functional electroceramics as an effective sintering aid [18]. Due to its low melting point, it is naturally accepted that liquid phase sintering is responsible for enhanced densification, but its evolution and role in promoting the densification during the sintering processing have not been clarified.

In the present work, complex multicomponent $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ perovskite microwave ceramics doped by 0.5 wt% CuO were strategically chosen as a model system. This study aims to elucidate the sintering behavior involved in the synthesis and processing of technologically important electroceramics. The structure and chemistry of grain boundary quasi-liquid layers in CuO-doped $0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ ceramics were identified. The relationship between their stabilization and densification behavior was clarified.

$0.7\text{CaTiO}_3\text{-}0.3\text{NdAlO}_3$ ceramics were prepared by conventional solid state reaction method aided by high energy milling technique. High purity CaCO_3 , TiO_2 , Al_2O_3 , and Nd_2O_3 (>99.99%) were used as raw powders. After they were mixed with ZrO_2 milling balls in a nylon jar using ethanol as milling media at a rate of 300 rpm for 14 h, they were re-milled at a rate of 500 rpm to refine particle size. CTNA ceramic powders were synthesized by calcining as-milled powders at 1350 °C for 10 h. Then, as-synthesized CTNA powders and 0.5 wt% CuO were mixed with binders (5 wt% paraffine and 1 wt% stearic acid) and pressed into cylindrical pellets of 5 mm diameter and 10 mm thickness. Isothermal sintering and constant-heating-rate (CRH) sintering

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were performed by dilatometer (DIL402PC, NETZSCH) to determine the sintering behavior and densification mechanism. Isothermal sintering was performed at soaking temperatures in a range of 1100–1150 °C for 3 h with a heating rate of 10 °C/min. In contrast, constant-heating-rate sintering was carried out at 1500 °C with a heating rate of 5 °C/min.

0.7CaTiO₃–0.3NdAlO₃ ceramics doped by 0.5 wt% CuO, which were sintered at 1100–1150 °C for one minute and one hour, respectively, were treated by water quenching to freeze up the structure and chemistry of the grain boundaries formed at elevated sintering temperature. They were further characterized by the Transmission Electron Microscopy (TEM) with spherical aberration correction (TECNAI G2 60–300, FEI). Specimens for TEM observation were prepared by mechanically grinding to ~50 μm and followed by ion-milling. Simultaneous Thermal Analyzer (Setsys evolution, SETARAM) was applied to reveal the phase transition of CuO during the sintering processing. Dielectric constant (ϵ_r) and quality factor ($Q \times f$) at microwave frequency were measured by network analyzer (N5230A, Agilent) using Hakki–Coleman dielectric resonator method [21] modified by Courtney [22]. Temperature coefficient of resonance frequency (τ_f) was measured by open-cavity method using invar cavity, in a temperature range from 25 to 85 °C.

Fig. 1 shows the density and densification rate as a function of heating temperature for undoped and 0.5 wt% CuO doped CTNA ceramics. It is observed that onset densification temperature (T_{onset}) occurs at a temperature of as low as ~930 °C for 0.5 wt% CuO doped CTNA ceramics. In contrast, it is ~1050 °C for undoped CTNA ceramics. Additionally, it is revealed that maximum densification rate temperature (T_{max}) is 1287 °C for 0.5 wt% CuO doped CTNA ceramics as opposed to 1442 °C for undoped ones. These results imply that doping CuO can significantly decrease the densification temperature of CTNA ceramics and shorten the soaking time needed to achieve high sintering density.

It is of interest to observe that an extra peak centered at ~1045 °C appears in the curve of 0.5 wt% CuO doped CTNA ceramics, as shown in Fig. 1, implying that an abnormal densification processing occurs. This peak is considered to originate from the appearance of grain boundary quasi-liquid Cu₂O–CuO layers evidenced by TEM images below. We would like to mention that XRD patterns (not shown here) show that the crystal structure of 0.5 wt% CuO doped CTNA ceramics is still of single phase perovskite and no detectable secondary phases are observed.

It is widely believed that the sintering processing is divided into densification stage and non-densification stage (grain growth and pores elimination) [23]. In this study, only the densification stage is considered. Therefore, both isothermal and constant-heating-rate sintering experiments were performed well below maximum

densification rate temperature (T_{max}). Under the assumption that only grain boundary and volume diffusion are taken into consideration, Bannister [24] suggests a general sintering kinetic equation for isothermal early-stage sintering:

$$\begin{aligned} \left(\frac{\Delta L}{L_0}\right)^{(n+1)} &= A_0 * \exp\left(-\frac{Q}{RT}\right) * t \text{ or } (n+1) \ln\left(\frac{\Delta L}{L_0}\right) \\ &= \ln t + \ln A_0 - \frac{Q}{RT} \end{aligned} \quad (1)$$

where $\Delta L/L_0$ is relative shrinkage, t is heating time, A_0 is a constant at fixed temperature, R is ideal gas constant (8.32J/mol K), T is sintering temperature, Q is apparent activation energy, and n is kinetic exponent, a featured value used to reveal the densification mechanism. The kinetic exponent n can be further derived by plotting the $\ln t$ against $\ln(\Delta L/L_0)$. Usually, $n = 0$ denotes that the sintering processing is dominated by viscous flow mechanism. In contrast, $n \sim 2$ and $n \sim 1$ indicate that the sintering processing is dominated by grain boundary diffusion and volume diffusion mechanism, respectively [24,25]. The natural logarithmic of sintering time and relative shrinkage is plotted in Fig. 2(a). It is observed that grain boundary diffusion dominates the sintering processing of undoped CTNA ceramics. In contrast, the sintering processing is dominated by viscous flow for 0.5 wt% CuO doped CTNA ceramics, a phenomena which usually occurs in the liquid phase sintering. However, we would like to point out that the sintering mechanism of CuO doped CTNA ceramics is strongly dependent on the sintering temperature and soaking time. When 0.5 wt% CuO doped CTNA ceramics are sintered at 1100 °C, its sintering mechanism changes from viscous flow to volume diffusion when soaking time increases. With lengthening soaking time for ceramics sintered at 1150 °C, it

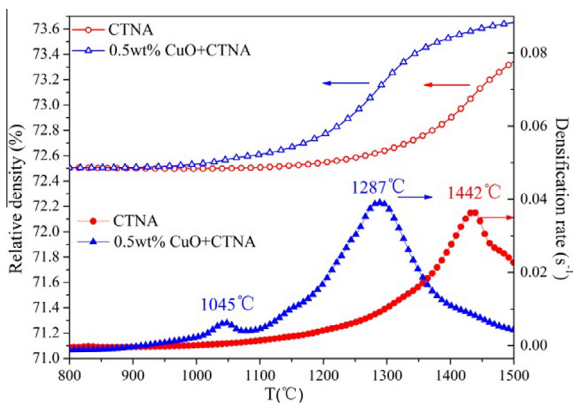


Fig. 1. Temperature dependence of the relative density and densification rate for 0.5 wt% CuO doped 0.7CaTiO₃–0.3NdAlO₃ ceramics.

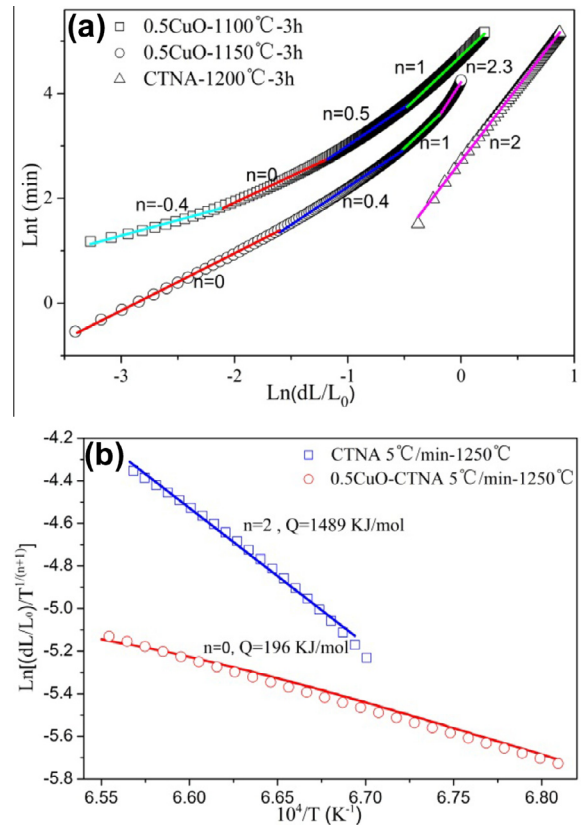


Fig. 2. Densification processing of 0.5 wt% CuO doped 0.7CaTiO₃–0.3NdAlO₃ ceramics: (a) index of dominant densification mechanism; (b) activation energy of viscous flow.

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