The effects of CuO addition on phase composition, microstructure, sintering behavior, and microwave dielectric properties of 0.80Sm(Mg 0.5Ti0.5)O3-0.20Ca0.8Sr0.2TiO3 (8SMT-2CST) ceramics prepared by a conventional solid-state ceramic route have been studied. CuO addition shows no obvious influence on the phase of the 8SMT-2CST ceramics and all the samples exhibit pure perovskite structure. Appropriate CuO addition can effectively promote sintering and grain growth, and consequently improve the dielectric properties of the ceramics. The sintering temperature of the ceramics decreases by 50 °C adding 1.00 wt.%CuO. Superior microwave dielectric properties with a \(e_r\) of 29.8, \(Q_f\) of 85,500 GHz, and \(s_f\) of 2.4 ppm/°C are obtained for 1.00 wt.%CuO doped 8SMT-2CST ceramics sintered at 1500 °C, which shows dense and uniform microstructure as well as well-developed grain growth.

Key words: Dielectric properties, 0.80Sm(Mg 0.5Ti0.5)O3-0.20Ca0.8Sr0.2TiO3 ceramics, CuO addition, quality factor

INTRODUCTION

With the development of modern communication systems, microwave dielectric ceramics have been a hotspot in the past two decades. In general, dielectric ceramics for microwave applications should meet three conditions: reasonable dielectric constant (\(e_r\)), low dielectric loss (high quality factor \(Q_f\)), and near-zero temperature coefficient of resonant frequency (\(s_f\)). These enable small size, prominent frequency selectivity, and high temperature stability for microwave devices, respectively. Recently, Ln(Mg0.5Ti0.5)O3 (La, Sm, Nd, Dy, Y) ceramic systems, owing to their excellent dielectric properties (\(e_r\) = 22–29, \(Q_f\) = 33,700–75,500 GHz, \(s_f\) = 65–6 ppm/°C) have been studied by many researchers. Apparently, however, the absolute value of their \(s_f\) is still too large, which limits their potential applications as dielectric ceramics.

Many reports have indicated that combining two ceramics which possess positive and negative \(s_f\), respectively, in an appropriate proportion could yield a new solid solutions or composite dielectric material with near-zero \(s_f\). For example, the \(s_f\) of La(Mg1/2Ti1/2)O3 is −65 ppm/°C and 0.55CaTiO3-0.45La(Mg1/2Ti1/2)O3 ceramics (sintered at 1450 °C for 6 h) exhibit a \(s_f\) of 1.06 ppm/°C, a \(e_r\) of 44.6, and a \(Q_f\) of 32,000 GHz. A \(s_f\) of 10.7, a \(Q_f\) of 35,000 GHz, and a \(s_f\) of −4.7 ppm/°C were obtained for 0.5La(Mg1/2Ti1/2)O3-0.5Ca0.8Sr0.2TiO3 ceramics sintered at 1475 °C for 4 h. The \(s_f\) of Nd(Mg1/2Ti1/2)O3 is −49 ppm/°C. A \(s_f\) of −3 ppm/°C, a \(e_r\) of 45.4, and a \(Q_f\) of 44,000 GHz were obtained for 0.1SrTiO3-0.9Nd(Mg1/2Ti1/2)O3 ceramics sintered at 1475 °C for 4 h. Among Ln(Mg0.5Ti0.5)O3 ceramic system, Sm(Mg0.5Ti0.5)O3 has a relatively high dielectric constant (\(e_r\) ~ 25), a high quality factor (\(Q_f\) ~ 65,500 GHz), and a negative temperature coefficient of resonance frequency (\(s_f\) ~ −26 ppm/°C), which has not been paid much attention because of its high sintering temperature. With a much higher \(Q_f\) than CaTiO3, Ca0.5Sr0.2TiO3 (\(e_r\) ~ 181, \(Q_f\) ~ 8,000 GHz, \(s_f\) ~ 991 ppm/°C), can be chosen as an ideal \(s_f\) compensator of Sm(Mg0.5Ti0.5)O3 ceramics. We found that the \(s_f\) of 0.80Sm(Mg0.5Ti0.5)O3-0.20Ca0.8Sr0.2TiO3 (hereafter referred to as 8SMT-2CST)
ceramics could be between –10 ppm/°C and 10 ppm/°C. However, a sintering temperature as high as 1550°C is necessary to obtain fully dense 8SMT-2CST ceramics.

To lower the sintering temperature of microwave dielectric ceramics, two methods are generally used, i.e., liquid phase sintering by adding materials with low melting points, preparing powders with high activation energy and small particle size by chemical processing methods or a mechanical method. The second method is usually complex, expensive, and time-consuming. Adding low melting-temperature materials such as CuO, B\textsubscript{2}O\textsubscript{3}, and V\textsubscript{2}O\textsubscript{5} is an effective and cheap way to achieve this purpose. Huang et al. reported the sintering temperature of Nd(Zn\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3} ceramics decreased by approximately 60°C when 0.75 wt.%CuO was added. Chen et al. found that the sintering temperature of 0.4Nd(Mg\textsubscript{0.4}Zn\textsubscript{0.1}Sn\textsubscript{0.5})O\textsubscript{3}-0.6Ca\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3} ceramics was reduced by around 250°C by adding 0.5 wt.%B\textsubscript{2}O\textsubscript{3}. In this work, CuO was chosen as an addition to lower the sintering temperature of 8SMT-2CST ceramics. Effect of CuO addition on sintering performance, microstructure and microwave dielectric properties of 8SMT-2CST ceramics was investigated. The results indicated that a reduction of 50°C in sintering temperature and excellent microwave dielectric properties ($\varepsilon_r = 29.8$, $Q\times f = 85,500$ GHz, $\tau_f = 2.4$ pm/°C) could be achieved by adding 1.00 wt.%CuO to 8SMT-2CST ceramics.

**EXPERIMENTAL PROCEDURE**

0.80Sm(Mg\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3}-0.20Ca\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3} ceramics were prepared by the conventional solid-state method. The starting materials were high-purity (>99%) Sm\textsubscript{2}O\textsubscript{3}, MgO, TiO\textsubscript{2}, CaCO\textsubscript{3}, and SrCO\textsubscript{3}. At first, Sm(Mg\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3} and Ca\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3} powders were synthesized by mixing the relevant starting materials according to the desired stoichiometry, ball milling for 6 h with zirconia balls, drying and calcining at 1100°C for 2 h and 1100°C for 4 h, respectively. Then, the synthesized Sm(Mg\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3} and Ca\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3} powders (on the basis of 0.80Sm(Mg\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3}; 0.20Ca\textsubscript{0.8}Sr\textsubscript{0.2}TiO\textsubscript{3}), as well as different amounts of CuO were re-milled for 6 h. After drying, the powders were pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under the pressure of 300 MPa, and then the pellets were sintered at 1450–1550°C for 3 h in air.

The phases of the samples were identified by x-ray diffraction (XRD; RIGAKU SmartLab(3)) using Cu K\textalpha radiation. The microstructure of the polished and thermal etched surface of the specimens was observed by a scanning electron microscopy (SEM; JEOL, JSM-5900). The bulk density of the samples was measured by Archimedes method. The dielectric properties of the samples at microwave frequency were measured by a network analyzer (Agilent 8722ET), using the modified Hakki and Coleman’s method. $\tau_f$ was evaluated in a temperature range from 25°C to 80°C.

**RESULTS AND DISCUSSION**

**Fig. 1.** XRD patterns of 8SMT-2CST ceramics with different CuO addition sintered at 1500°C for 3 h.

**Fig. 2.** XRD patterns of 8SMT-2CST ceramics with 1.00 wt.% CuO addition sintered at different temperatures for 3 h.