Synthesis and microwave dielectric properties characterization of $Ca_{1-x}Mg_xTiO_3$ ceramics

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Abstract

Solid solutions of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) were prepared via conventional solid state route. The microwave dielectric properties and density of the fabricated samples were measured. The XRD patterns of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) recorded at room temperature indicates two phase perovskite structured material. The SEM images indicated dense ceramic with no pores and round shape grain morphology. The dielectric constant (ε_r) increased to 124.43 with Mg^{2+} doping and maximum dielectric constant was observed for $Ca_{0.8}Mg_{0.2}TiO_3$ while the quality factor ($Q \times f_o$) of $Ca_{0.4}Mg_{0.6}TiO_3$ reaches to 2000 MHz whereas pure $CaTiO_3$ posses relatively smaller quality factor ($Q \times f_o \sim$ 1333.33 MHz). The dielectric constant was found to be directly proportional to the density of samples. All measurements were taken at room temperature at relatively lower frequency of 2 MHz.

Key words: Perovskites, Dielectric resonator, Microwave dielectrics, mixed oxides

Introduction

Development in microwave (MW) technology and telecommunication industry have led to the rapid growth of wireless communication and information systems during the last several years (Ali et al. 2020; Chen et al. 2004; Huang & Liu 2007; Okaya & Barash 1962; Reda et al. 2016; Richtmeyer 1939; Zaman et al. 2021). The development of cellular mobile phone and enormous increase in the number of its users is an example of its wide application (Cava 2001). Ceramics with perovskite structures are widely used as microwave dielectric components in the telecommunication industry (Freer & Azough 2008). Ceramic dielectrics with specific combination of different properties make these suitable for microwave applications as dielectric resonators (DRs) (Takata & Kageyama 1989). A dielectric resonator (DR) is a non-metalized component made of ceramics and is able to resonate at a particular frequency of the carrier signal to allow that signal to be efficiently separated from other unwanted signals. The frequency at which a DR resonates is called the resonant frequency (Zaman et al. 2021). The word ‘‘dielectric resonator’’ initially appeared

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in 1939, when Richtmeyer from Stanford University reported that a suitably shaped dielectric piece can work as a microwave resonator (Richtmeyer 1939). However, it took more than 20 years to make further interest on DRs and to confirm Richtmeyer's prediction experimentally. In 1953, Schlicke (Schlicke 1953) studied super high permittivity materials (~1000 or greater) and their applications as capacitors at relatively low frequencies.

The desired characteristics for a dielectric resonator are; relative permittivity ($\varepsilon_r \sim 80$), quality factor ($Q \times f_o \sim 5000$ GHz) and near zero temperature coefficient of resonance frequency ($\tau_f = 0$ ppm/°C). High dielectric constant of dielectric materials can lead to the miniaturization of electronic circuits. High quality factor is important for less loss and near zero τ_f indicates thermal stability of a DR (Chen et al. 2004; Huang & Liu 2007; Okaya & Barash 1962).

Perovskite structured calcium titanate ($CaTiO_3$) shows high quality factor ($Q \times f_o \sim 7000$ GHz) and dielectric constant ($\varepsilon_r \sim 160$) but undesired high $\tau_f \sim 805$ ppm/°C (Cava 2001). On the other hand $MgTiO_3$ is reported to exhibit good dielectric properties of $\varepsilon_r \sim 17$, $Q \times f_o \sim 160{,}000$ at 7 GHz and $\tau_f \sim -50$ ppm/°C (Samyuktha 2017). The doping of Mg^{2+} in $CaTiO_3$ for Ca^{2+} can decrease its τ_f .The perovskite structure is one of the most extensively studied structures in materials science. German mineralogist and chemist Gustav Rose discovered the mineral $CaTiO_3$ in 1839. Rose named $CaTiO_3$ after Lev Alexeievitch Perovsky, an official and dignitary in Russian military. The atomic arrangement for ABO_3 perovskite structure was first observed for the mineral perovskite $CaTiO_3$ (Courtney 1970; Molla 1999). In the present work the effects of Mg^{2+} doping on phase, microstructure and MW dielectric properties of $CaTiO_3$ were investigated.

Experimental procedure

In the present research mixed oxides, solid-state route was used to fabricate Solid solutions of $Ca_{1-x}MgxTiO_3$ ($0 \leq x \geq 0.8$). High purity materials such as $CaCO_3$ (99% purity, Sigma Aldrich), TiO_2 (99.4% purity, Sigma Aldrich) and $MgCO_3$ (99.6% purity, Sigma Aldrich) were used as starting materials. These materials were taken according to the stoichiometry and mixed /milled uniformly for 24h via horizontal ball mill. Samples were calcined at 950°C for 2h at the heating and cooling rates of 10°C/min while sintered at 1400°C for 2h at the heating and cooling rates of 20°C/min. The phase analyses were carried out by X-Ray diffractomete (XRD). The densities of samples were calculated using Archimedes principle by densitometer. The microstructures of

samples were studied by scanning electron microscope (SEM). The dielectric properties were measured by LCR meter.

An LCR meter was used for capacitance and tanδ measurements. The measurements were carried out at room temperature. Samples were placed in a non-conductively wound tube furnace and measurement were be taken.

Results and discussion

Phase Analysis

The phase analysis of samples was carried out by X-ray diffraction spectroscopy. The XRD patterns (Figs. 1(a, b)) of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) recorded at room temperature indicates two phase perovskite structured (Samyuktha 2017). $CaTiO_3$ matching with PDF card number (22-153) while $MgTiO_3$ matches with PDF card no (79-831). Figure 13(b) shows the shifting of the 200 peak towards lower 2θ values which is attributed to the substitution of relatively smaller Mg^{2+} ion at the 12 fold coordinated A-site of the perovskite structure relative to Ca^{2+} ion (Sabastian et al. 2015). Since the ionic size of Calcium was greater than Magnesium, the magnesium Titanate was formed as an additional phase showing rhombohedral structure whereas Calcium titanate shows orthorhombic structure. The ionic radius of Ca^{2+} and Mg^{2+} are 1.34 Å and 0.89 Å respectively (Shannon 1976). The size difference is visible in form of minor shift in XRD patterns following the Braggs diffraction law.

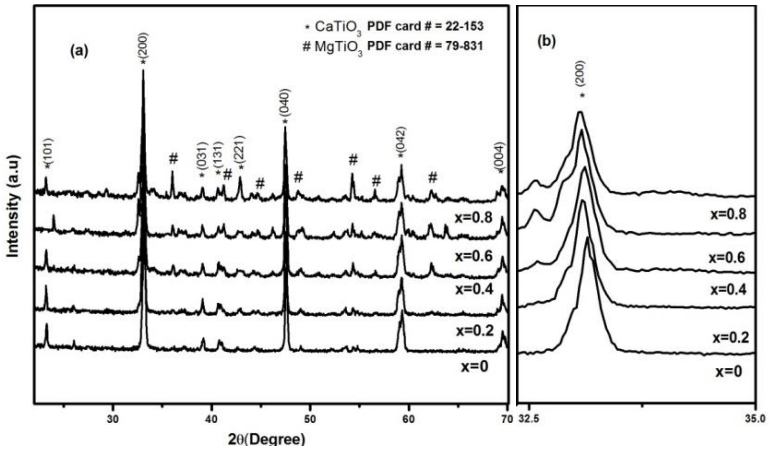

Figure 1. (a) XRD pattern of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) calcined at 950 °C (b) shifting of (200) plane toward lower 2θ values.

Density measurement

Densities of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) ceramic samples were measured by using densitometer as shown in Fig. 2. Variation in density was observed for various substitution of Mg^{2+}. The density of the processed ceramic is first increased for x = 0.2 and then gradually decreased. The Maximum density (3.83 g/cm^3) was recorded for $Ca_{1-x}Mg_xTiO_3$ (x = 0.2). Fig. 5 and Fig. 3 indicated that dielectric constant is directly proportional to the density.

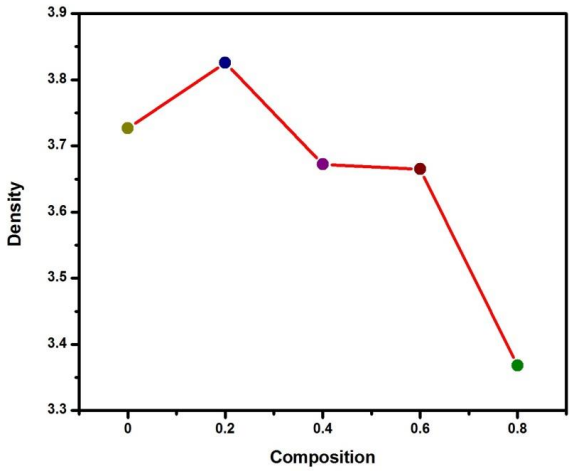

Figure 2. Variation of Density with "x"

Microstructural analysis

The surface morphology of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) sintered at 1400 °C were investigated by Scanning Electron Microscopy (SEM) as shown in Figure 3. SEM images of polished samples revealed dense ceramics with no obvious pores. The morphology of the grains is of spheroidal shape and of about 5 x 5 μm^2 in size. The grain size of sample is increased with substitution of Mg^{2+} (Fig. 3(b)).

Microwave Dielectric Properties

The MW dielectric properties of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) were measured using LCR meter. The capacitance and tanδ were measured at relatively lower frequency of 2 MHz. Measurements were taken at room temperature in non-conductive wound tube furnace. The optimum value of dielectric constant (ε_r) is found for $Ca_{1-x}Mg_xTiO_3$ (x = 0.2) that is 124.43 which is greater than all other compositions even

greater than $CaTiO_3$ having comparatively smaller ε_r ~109 as shown in Fig 4.

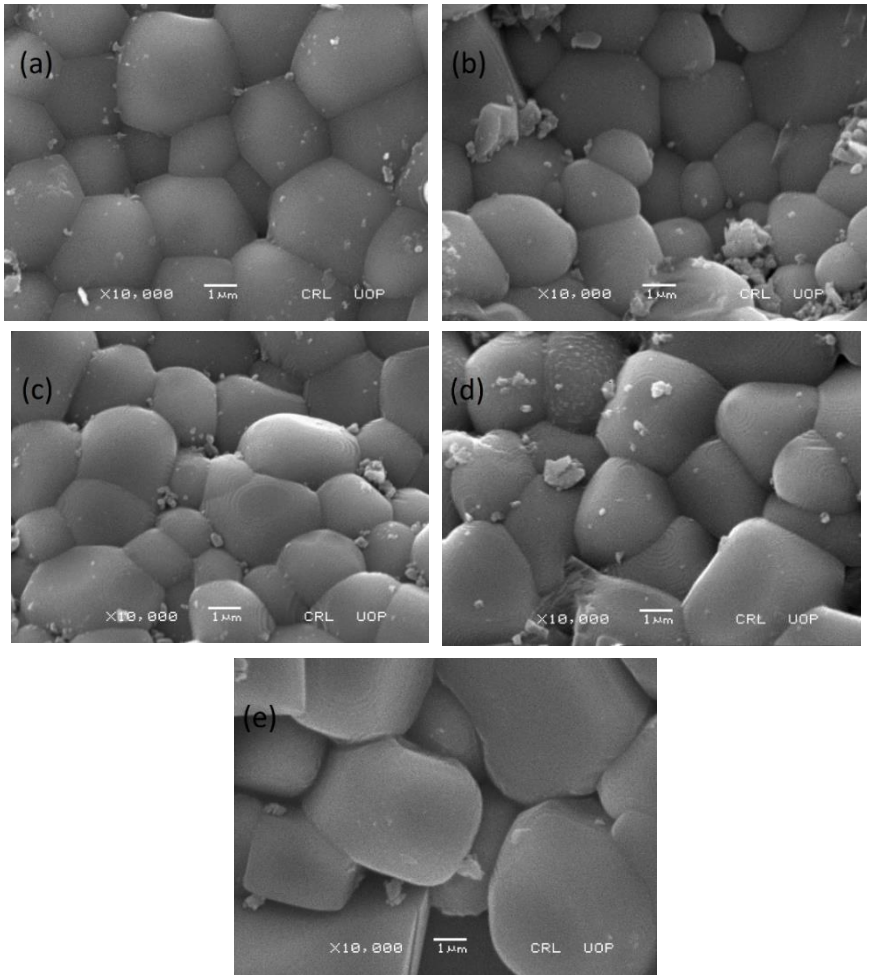

Figure 3. SEM images of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) sintered at 1400 °C in air (a) x = 0 (b) x = 0 (c) x = 0.4 (d) x = 0 .6 (e) x = 0.8

The quality factor ($Q \times f_o$) of $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) is measured at relatively lower frequency of 2 MHz and at room temperature in non-conductive wound tube furnace. The maximum value of quality factor is found for x = 0.6 ($Q \times f_o$ ~ 2000 MHz) which is not enough for practical applications under the processing conditions employed in the present

study as shown in fig 5. The MW dielectric properties are consistent with the previous study (Sabastian et al. 2015). The substitution of Mg^{2+} ions for Ca^{2+} ions changed the $Q \times f_o$ values, probably due to distribution of cation at the A site of the perovskite structure and the reduction in volume of the cation sites. The volume of cation sites reduces with a decrease in ionic radius, and as a result the movement of cations decreases (Shannon 1976). The MW dielectric properties are listed in Table. 1.

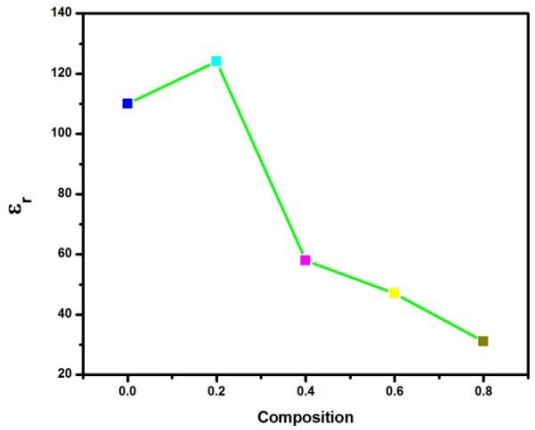

Figure 4. Variation of ε_r with "x"

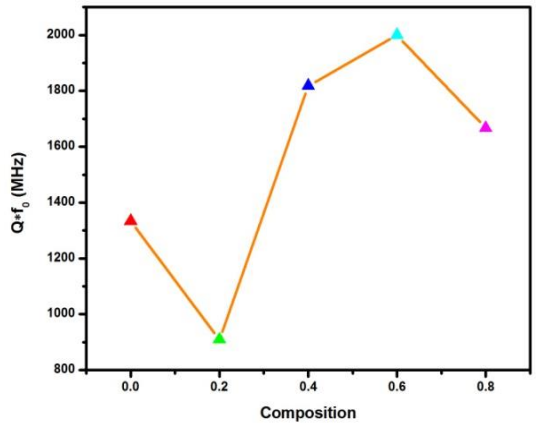

Figure 5. variation of $Q \times f_0$ with "x"

Table 2. Comparison of MW dielectric properties of fabricated samples at 2 MHz frequency.

X	C.T. (°C)	S.T. (°C)	ρ (g/cm³)	(ε_r)	Tan δ	Q	Q×f_o (MHz)
0	950	1400	3.727	109	0.0015	666.66	1333.33
0.2	950	1400	3.826	124	0.0022	454.54	909.09
0.4	950	1400	3.672	58.273	0.0011	909.09	1818
0.6	950	1400	3.665	47.908	0.0010	1000	2000
0.8	950	1400	3.368	30.864	0.0012	833.33	1666.66

C.T.: Calcination Temperature, S.T.: Sintering Temperature, ρ: Density, ε_r : Relative Permittivity, Tan δ : Dielectric loss, Q: Quality Factor, f_o : Frequency.

Conclusion

Single phase $Ca_{1-x}Mg_xTiO_3$ ($0 \leq x \geq 0.8$) ceramic samples were prepared via conventional solid state route. The microwave dielectric properties and density of the fabricated samples were measured. The SEM images indicated dense ceramics. The maximum dielectric constant was observed for $Ca_{0.8}Mg_{0.2}TiO_3$ while the quality factor ($Q \times f_o$) of $Ca_{0.4}Mg_{0.6}TiO_3$ reaches to 2000 MHz. The quality factor of pure $CaTiO_3$ was equal to 1333.33 MHz.

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