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Effect of Calcium Titanate Addition on the Phase, Microstructure, and Microwave Dielectric Properties of $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})O_3$ Ceramics Calcined at 1200 °C for 5h.

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Abstract

This study investigate the impact of adding calcium titanate ($CaTiO_3$) to $(Mg_{0.95}\ Co_{0.05})(Ti_{0.95}\ Sn_{0.05})O_3$ ceramics for wireless communication application. The ideal ceramics for these systems must three criteria: a near –zero τf value, a suitable dielectric constant for miniaturization, and an attractive unloaded quality factor (Qufo) for selectivity. The initial ceramics had a high negative τf value, which was improved by adding 6wt% $CaTiO_3$. The samples were synthesized using high- purity oxides and sintered at temperatures between 1325°C and 1425°C. X-ray diffraction (XRD) revealed three phases: $(Mg_{0.95}\ Co_{0.05})(Ti_{0.95}\ Sn_{0.05})O_3$, $CaTiO_3$, and $MgTi_2O_5$. The densest sample, sintered at 1400°C, achieved a bulk density of $3.86 g/cm^3$. Results showed that the addition of $caTiO_3$ improved τf by 40 ppm/°C, and increased the dielectric constant (εr) to 19.3. However, it reduced the Qufo value to 128,000 GHz. The final material demonstrated promising microwave dielectric properties.

Introduction

The word ceramics comes from ancient Greek word "keramikos" and the meaning of keramikos is burnt substance. As it is clear from its meaning; ceramics are obtained from heating the materials to high temperature for getting the required properties of the solid ceramics' materials [1]. Ceramics are inorganic, nonmetallic compounds made from metallic and nonmetallic elements with ionic, covalent, or mixed bonding. Their high strength surpasses metals due to the strong atomic bonds within their structure [2]. Ceramics are dielectric, resisting charge flow while allowing polarization. They prevent short circuits in electrical circuits, serve as insulators in capacitors, and function as dielectric resonators in telecommunication devices for decades. [3]. When dielectric solid ceramics materials are used in the external electric filed, they have no transport of charges but they only have some degree of arrangement of charges and the material is said to be polarized [4]. All the solid ceramics materials which are used in the past centuries and in the 21 centuries can be divided in two key groups. Traditional ceramics (like tiles, bricks, etc.) for which the essential raw material is clay Highly developed solid ceramics which take part in modern technologies (like: wireless communication applications, energy density storage, etc.) of the present era [5]. Before solid ceramics, large air-filled resonators were used, but their size was problematic. The discovery of TiO_2, with a high dielectric constant, enabled device miniaturization, leading to advanced solid ceramics research [6]. The discovery of TiO_2, despite its high temperature coefficient (τf = 450 ppm/°C), sparked interest in materials with high dielectric constants, replacing air-filled resonators. Post-1960, ceramics with high εr, Qufo, and near-zero τf were developed, revolutionizing wireless communication devices. Key properties for practical use include near-zero τf, high Qufo, and suitable εr for device miniaturization [7]. This research aimed to miniaturize devices, focusing on dielectric constant as the key property for size reduction. Since TiO_2's discovery in 1960, solid ceramics have been classified into three groups based on their dielectric constants for wireless communication applications [8]. $MgTiO_3$, a key ceramic material reported by K. Wakino in 1989, exhibits attractive properties: εr ~ 17, Qufo ~ 16×10^4 GHz at 7 GHz, and τf ~ −50 ppm/°C. However, its high $_{negative}$ τf limited practical use. To address this, $CaTiO_3$ (εr ~ 170, Qufo ~ 36×10^2 GHz, τf ~ +800 ppm/°C) was added as a τf compensator, enabling applications in GPS, radar, filters, and oscillators [9]. Adding 5wt% $CaTiO_3$ to $MgTiO_3$ achieved optimal properties: εr ~ 20, near-zero τf, and Qufo ~ 56,000 GHz at 7 GHz. Similarly, C.L. Huang (2010) reported improved properties with 7wt% $CaTiO_3$ in Mn-doped $MgTiO_3$: Qufo ~ 90,700 GHz, εr ~ 22.67, and τf ~ +0.8 ppm/°C. MgTi0.95Sn0.05O3 also faced challenges due to its unsuitable τf (−43 ppm/°C) for practical applications [10].This defect was removed from the aforementioned material in 2018 by J. Iqbal and his research team with the addition of high positive $\square_f$ value material (i.e., $Ca_{0.8}Sr_{0.2}TiO_3$ ceramics: $\square_f$ ~ + 991 ppm/°C). The reported $\square_f$ value of (1−x) $MgTi_{0.95}Sn_{0.05}O_3$− $xCa_{0.8}Sr_{0.2}TiO_3$ solid ceramics was − 1.79 ppm/°C, which was in the range needed for the use in the practical wireless communication devices [11]. The same team addressed material defects by adding CaTiO3, though the quality factor was slightly lower. C.L. Huang used Ca0.8Sr0.2TiO3 to adjust τf from −65 to 0.1 ppm/°C in $(Mg0.7Zn0.3)_{0.95}Co_{0.05}TiO_3$, achieving τf ~ 0.10 ppm/°C, Qufo ~ 90,000 GHz at 8 GHz, and εr ~ 22.5 [12]. In 2009, researchers adjusted the τf of ($Mg_{0.95}Ni_{0.05}TiO_3$) by adding $Nd_{0.5}Na_{0.5}TiO_3$, reducing it from −45 to −6 ppm/°C. In 2018, A. Manan reported $(Mg_{0.95}Ni_{0.05})(Ti_{0.98}Zr_{0.02})TiO_3$ with εr ~ 17, Qufo ~ 195,000 GHz, and τf ~ −46 ppm/°C [13].The high negative τf value made the material impractical, so $Ca_{0.6}La_{0.8/3}TiO_3$ (εr ~ 109, Qufo ~ 17,000 GHz, τf ~ 212 ppm/°C) was added to $(Mg_{0.95}Ni_{0.05})(Ti_{0.98}Zr_{0.02})TiO_3$. The optimal composition, $0.85(Mg_{0.95}Ni_{0.05})$ $(Ti_{0.98}Zr_{0.02})TiO_3$ – $0.15Ca_{0.6}La0_{.8/3}TiO_3$, improved τf to −2 ppm/°C, increased εr to 23.9, and achieved a density of 3.86 g/cm³. In 2018, A. Manan et al. developed $(Mg_{0.95}Ni_{0.05})(Ti_{0.98}Zr_{0.02})TiO_3$ ceramics with εr ~ 17, Qufo ~ 195,000 GHz, and τf ~ −46 ppm/°C. To address impractical τf, $Ca_{0.6}La_{0.8/3}TiO_3$ (εr ~ 109, Qufo ~ 17,000 GHz, τf ~ 212ppm/°C) was added [14]. By adding $Ca_{0.6}La_{0.8/3}TiO_3$ to $(Mg_{0.95}Ni_{0.05})(Ti_{0.98}Zr_{0.02})TiO_3$, the optimal composition $0.85(Mg_{0.95}Ni_{0.05})(Ti_{0.98}Zr_{0.02})TiO_3$ – $0.15Ca0.6La0.8/3TiO_3$ improved τf to −2 ppm/°C, raised εr to 23.9, and achieved a density of 3.86 g/cm³. In 2015, H. J. Jo et al. reported $Mg(Ti_{0.95}Sn_{0.05})O_3$ with εr ~ 17.7, Qufo ~ 276,000 GHz, and τf ~ −43 ppm/°C [15].The τf value (−43 ppm/°C) was unsuitable for practical wireless applications, affecting circuit efficiency. In 2017, J. Iqbal's team eliminated this defect using the mixing route method with calcium titanate as a τf compensator [16].The research group added a positive τf compensator in ratios (0.02 ≤ x ≤ 0.08) to the main composition, sintering at 1300–1400 °C for 4h. At 1375 °C, optimal density (~3.8 g/cm³) and microstructure were achieved. A secondary CaTiO3 phase improved τf (1.1 ppm/°C) and εr (~21.5) but reduced Qufo (~112,500 GHz) [17]. Huang's team optimized $Mg_4Nb_2O_9$ − $SrTiO_3$ ceramics, raising the τf value from -70 to 1.6 ppm/°C. Increased compensator ratio improved density (max 4.6 g/cm³), εr (21.02), and τf, while slightly degrading Qufo (112,000 GHz) Sintering at 1300°C/4h yielded optimal microwave dielectric properties[18].They added $CaTiO_3$ compensator (0.05 ≤ x ≤ 0.08) to $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics with 7 wt% $CaTiO_3$, τf improved from −54 ppm/°C to −1.4 ppm/°C, and εr increased from 16.8 to 21.6, while Qufo decreased from 230,000 GHz to 92,000 GHz. Optimal properties were achieved at 1275 °C/4h for $0.93(Mg0.95Co0.05)TiO_3$ − $0.07CaTiO_3$ ceramics [19].

Experimental Procedures Processing of Solid Ceramics

currently a lot of methods have been developed by the researchers for the synthesis of solid ceramics which are needed for different uses and applications; however, the "solid state reaction method" is easy, cost effective, steady and stable approach among all the methods. The following are the steps which are followed by the researches during the solid-state route method:

Selection Of Raw Materials for The Preparation of Solid Ceramics Samples

For the solid dielectric ceramics synthesis finest, quality oxide powered (TiO_2, MgO, CaO, SnO_2. CoO ≥ 99.99 %) were used, and they serve as a reactant for specimens of $(Mg_{0.95}Co_{0.05}Ti_{0.95}Sn_{0.05})O_3$ and $CaTiO_3$ ceramic materials being fabricated independently.

Weighting of Oxides and Grinding of Raw Materials

After the appropriate weighing of all the oxides the powders were then combined according to their desired ratio. The combination of these oxides along with the solid sphere zirconia balls were deposited in the polyethylene bottles, which were then milled for 10 hours continuously by the machine known as ball milling machine as shown in fig. 1.1. After that mixture was then placed in the oven which was operating at temperature of 100 °C in-order to evaporate the propanol. The next step which was followed after evaporating the propanol from the oxides was to pass the dried oxides through mesh sieve having size of 200.

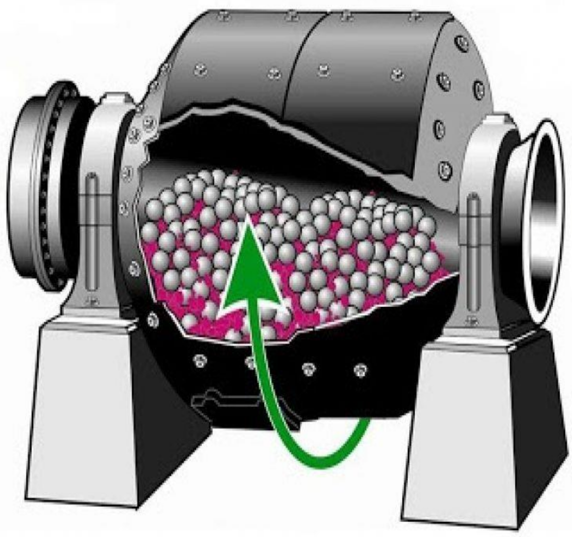

Fig. 1.1: Picture of Ball milling machine used for the milling of oxides.

Powder Calcination

The heating process which is used by the researchers in order to fade away/ volatile the unwanted chemicals or ingredients is known as calcination. The calcination is also called by the researchers as purification process. In the present research work the final solid ceramics powders were calcined at 1200 °C while using the heating and cooling rate of 5 °C/ min to get the preferred phases. After the conformation of the required phases the solid dried ceramics powders were again refilled in the plastic bottles using the zirconia balls for 24 hours. Before, the formation of solid ceramics pellets PVA was added. The solid ceramics powders were then pressed under pressure of 150 MPa in the dia having dimensions of 6 mm thick and 12 mm in diameter to get disk like samples. To eject the PVA from the cylindrical pellets were again heat treated in the furnace for 2 hours at temperature of 600 °C.

Sintering Method for Densification of the Samples

Since when the solid powders are initially pressed in the pellets form, then there is possibility of the having large number of pores inside the pellets and these pores are not good for the properties which are necessary for the wireless communication. In the present research work, to get the dense solid ceramics the samples of the solid 1-x $(Mg_{0.95}Co_{0.05}Ti_{0.95}Sn_{0.05})O_3$ -x $CaTiO_3$where x = 6 wt% ceramics materials were heated in the furnace in the temperature range of 1325 °C to 1425 °C with the stay time of 4h.

Polishing Technique

After sintering the all the solid ceramics samples were polished for the purposes to remove the undesirable elements.

Techniques For Characterization

The following discussed techniques were carried out of the sintered solid ceramics; in order to examine the solid material's dielectric characteristics, density, microstructures, and the phase's formation.

Density

Archimedes method was used in order to calculate the bulk densities of all the solid ceramics samples by adopting the below eq^n. and using the well-known equipment "density meter".

$$\rho_{bulk} = \frac{a_1}{a_3 - a_2} \qquad 1.1$$

Where in the afore eq^n. (1.1) a_1 shows the mass of the sintered solid ceramics pellets in air, a_2 denotes the pellet and thread mass when sink in water, and the last a_3 is the mass of the samples with thread in air.

For the compositions the below eq^n. was used to calculate the theoretical densities.

$$\rho_{theo} = \frac{ZA}{V_{Cell} \times N_A} \qquad 1.2$$

After the calculation of experimental and theoretical density of all the samples they were compared to get the relative densities of the solid ceramics samples using the following eq^n. 1.3.

$$\rho_{rel} = \frac{\rho_{bulk}}{\rho_{theo}} \times 100 \qquad 1.3$$

XRD

X-Rays diffraction machine is famous and broadly used by the researchers for the detection of structures in their prepared materials. The crystalline phases of the sintered ceramics were identified using X-ray diffraction (XRD; PANalytical Expert PRO). Bragg's law can be used to calculate the distance between the planes while taking the peak location and wavelength of the source of radiation into consideration as shown in diagram 1.2

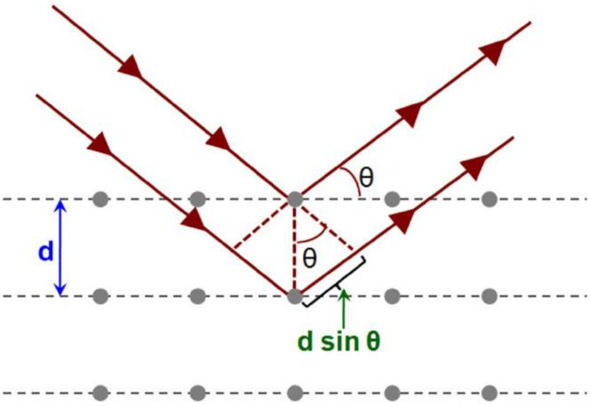

Diagram. 1.2: illustration of Bragg's law.

Bragg's law mathematical form:

$$n\,\lambda = 2d \,\mathrm{Sin}\,\theta \qquad 1.4$$

In the above equation, "d" denotes the distance between two planes, "λ" is the electromagnetic radiation's wavelength, "n" denotes the plane's order, and "θ" is the scattering angle.

Field Emission Scanning Electron Microscopy (FESEM)

Before the use of the FESEM all the sintered samples prepared in our lab were first polished well in order to make the surfaces of the samples smooth and also to remove the additional ingredients. Secondly, the samples which were chosen for the FESEM (JSEM-5610LV, Japan) were thermally etched for 30 minutes again at temperature which was about 100 °C less than the actual sintering temperature of all the solid ceramics samples. EDS (Energy-Dispersive X-ray Spectrometry) were used in order to get information about the microstructure of the prepared samples and also to identify the elemental composition.

Network Analyzer

The $\square_r$ and the quality factor value of the prepared samples were obtained using an Agilent 8722 (50 MHz to 40 GHz) network analyzer and the Hokki-Coleman dielectric resonator technique. The $\square_f$ value was calculated for the solid samples prepared in our lab by measuring the resonant frequency in the temperature range of 25-85 °C using eq^n 1.5.

$$\square_f = f_2 - f_1 \div f_1 \, (T_2 - T_1) \qquad 1.5$$

Where, in the above eq^n 1.5 the f_1 and f_2 represents the resonant frequencies at temperature T_1 (25°C) and temperature T_2 (85°C), respectively.

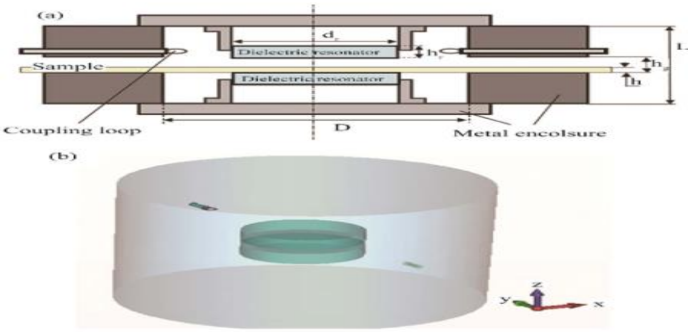

Fig. 1.3: Picture for the cylinder cavity resonance technique.

Results And Discussion

XRD Patterns of the Prepared Solid Ceramics

In the present experimental study, the XRD patterns of the final sintered solid 94$(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$– 6$CaTiO_3$ceramics at sintering temperatures of: 1325°C, 1350 °C, 1375 °C , 1400°C , & 1425°C were received using the X- Ray diffraction technique as shown in Fig. 1.4. The pattern revealed the development of peaks of three phases: (1) Magnesium titanate based ceramics represented by the symbol “ * ” in the figure, (2) Calcium titanate based ceramics represent by the symbol “ + ” in the figure, and (3) $MgTi_2O_5$ solid ceramics represented by the symbol “ # ” in the figure 4.1. Since, the mixture usually resulted in the formation of at least two phases when the ionic difference between the cations of the two added solid ceramics is too much. However, in the present study another minor phase was also detected in the XRD patterns, which is usually attained during the formation of magnesium titanate solid ceramics formation and is difficult to eradicate from the solid ceramics [20]. Moreover, from the peaks in the XRD patterns of the solid ceramics it was also observed that slight decrease was observed with the increase in the sintering temperature form 1325 °C to 1425 °C.

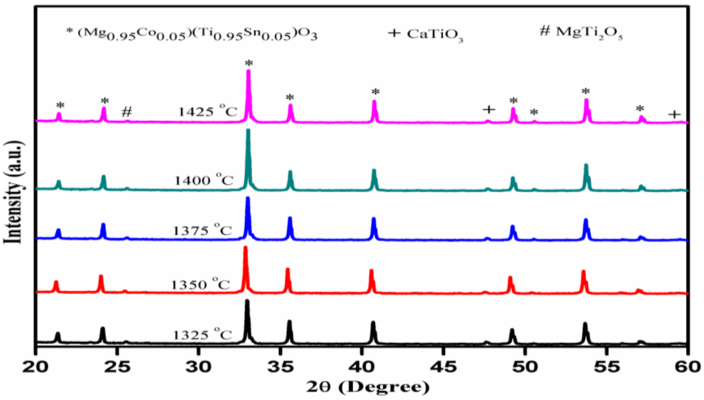

Fig. 1.4: XRD patterns of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3 - 6CaTiO_3$ceramics sintered for 4 hours at different temperatures.

Apparent Density of The Prepared Solid Ceramics

The apparent density of the solid ceramics is the main extrinsic factor which affects the overall microwave dielectric properties. Since, sintering temperature plays the key role in the densification of the solid ceramics material and is therefore affected too much by the sintering temperature. The well dense ceramics are usually attained at slight lower sintering temperature than the melting temperature of the solid ceramic's materials. With the elimination of the pores resulted in the enhancement of the apparent density of the solid ceramics. The lowest apparent density of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3 - 6CaTiO_3$ceramics was noted at the starting sintering temperature of 1325 °C. However, step wise rise was seen in the apparent density of the prepared solid ceramics with the further increase in the sintering temperature from 1325 °C. The reason behind the enhancement of the apparent density was attributed to the removal of the pores from the samples. The uppermost apparent density noted for the prepared ceramics in the present experimental study was 3.86 g/cm^3, which was accomplished at sintering temperature of 1400 °C as shown in Fig. 1.5. However, the further enhancement in the deriving temperature caused decline in the apparent density instead of further enhancement. At sintering temperature of 1425 °C the apparent density attained for the prepared solid ceramics were 3.83 g/cm^3, which is lower than that achieved at 1400 °C. From this behavior of the prepared solid ceramics apparent density it is also became evident that the perfect densification temperature for the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3 - 6CaTiO_3$ceramics is 1400 °C and beyond this deriving temperature melting or abnormal grain growth starts in the solid ceramics.

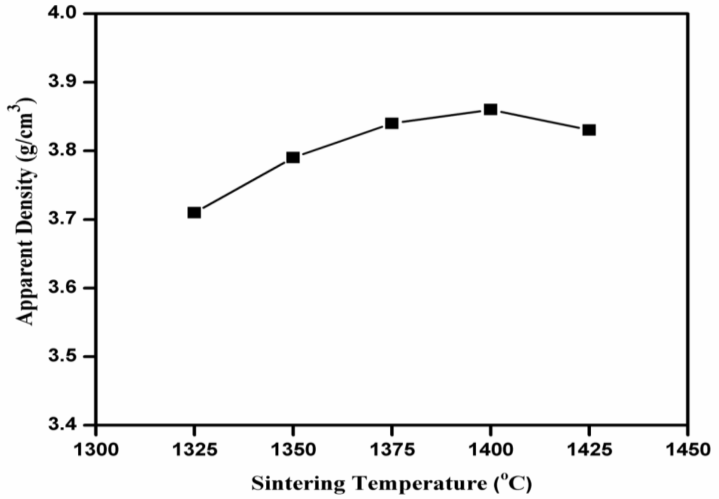

Fig 1.5: Sintering temperature effect on the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3 - 6CaTiO_3$ceramics apparent density.

Micrograph Of the Prepared Solid Ceramics

Figure 1.6, Shows the SEM micrograph of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$ceramics sintered at 1400 °C was collected using the FESEM. From the micrograph of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$ceramics it is evident that the pores are almost eliminated from the samples, that's why higher density was achieved at this sintering temperature. Moreover, the grains are uniform and no abnormal grain growth was detected. Additionally, three different types of grain were formed and detected in the micrograph of the solid ceramics sintered at 1400 °C. The reason behind the three types of grain formation is the existence of the three different types of materials formation in the prepared solid ceramics which were identified and confirmed in the XRD patterns. All the three grains were labeled with three capital alphabets as: "A" for the grain of magnesium titanate solid ceramics, "B" for the calcium titanate solid ceramics, and "C" for the $MgTi_2O_5$ solid ceramics as shown in figure. Javed at al. confirmed these grains by using the EDS technique in his research study on the magnesium titanate based ceramics and found that the large grains have Magnesium and Titania as 1:1 ratio and were confirmed as main magnesium titanate solid ceramics, while in the small rounded grains Calcium and Titania were in the 1:1 ratio and they referred as compensator calcium titanate grains, and the last "C" type grain which are rod type had also the magnesium and titania but were in the ratio of 1:2

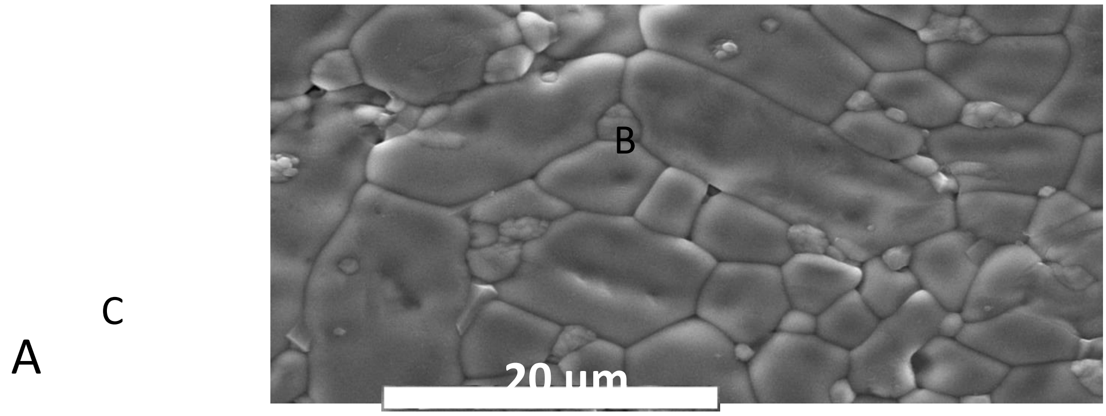

Fig. 1.6: SEM micrograph of the 6 wt% compensator added solid $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ ceramics sintered at 1400 °C.

Relative Permittivity of The Prepared Solid Ceramics

Figure 1.7 shows the relative permittivity of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$ceramics deviation with the sintering temperature in the range of 1325 °C to 1425 °C. The ε_r value of the solid ceramics is affected by the extrinsic factors like density, microstructure, pores, cracks, formation of secondary phases in the prepared ceramics, and the polarizability of the dopant's elements [21]. The ε_r of the presently prepared solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$ceramics was also noticed to be affected more by the extrinsic factors. Since the calcium titanate which is added as compensator has higher dielectric constant than that of the main composition magnesium-based ceramics; and this difference in the ε_r value of the two added solid ceramics in the ratio of 6:94 resulted a boost in the ε_r value of the magnesium titanate-based ceramics from 18 above. Moreover, the observed ε_r value of the prepared solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$ceramics was also seen to be affected too much by the sintering temperature. The worse value of 18.4 was attained for the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95Sn0.05})TiO_3-6CaTiO_3$ceramics at sintering temperature of 1325 °C. The ε_r value was noticed as 18.7 with the increase in the 25 °C rise in the sintering temperature and founded the same trend of enhancement with each time raise in the sintering temperature. The uppermost ε_r value was obtained at the sintering temperature of 1400 °C and the reason of the increase in the ε_r value was attributed to the exclusion of pores & densification of the solid ceramics. A sintering temperature of 1425 °C was noted as degradation sintering temperature for the ε_r value, after the continuous rise in the ε_r value with the sintering temperature. This fall in the ε_r value at 1425

°C was due to the decline in the apparent density at this temperature, which might be due to the abnormal grain growth and pores formation.

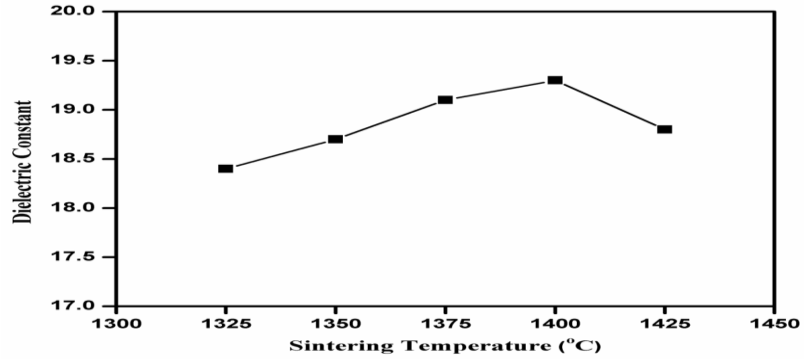

Fig. 1.7: Solid 94($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3− 6$CaTiO_3$ceramics relative permittivity deviation with the sintering temperature.

Quality Factor of the Solid Ceramics

Variation of the quality factor value with the sintering temperature of the presently prepared solid 94($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3− 6$CaTiO_3$ceramics is represented in figure 1.8. In the present study the Q_uf_o value of the solid 94($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3− 6$CaTiO_3$ceramics was much influence by the extrinsic factors because after the characterization of the solid ceramics samples extrinsic factors like the presence of the secondary phases and density variation with sintering temperature of the solid ceramics were noticed. Since, the solid ($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3 ceramics was initially reported to have higher Q_uf_o value of about 28.8 x 10^4GHz .After the addition of small amount of calcium titanate (Q_uf_o~3600 GHz at seven GHz) degraded a lot the Q_uf_o value of the final prepared solid 94($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3− 6$CaTiO_3$ceramics. Moreover, the presence of minor $MgTi_2O_5$ solid ceramics may also be the reason of the degradation in the Q_uf_o value of the final prepared ceramics. Additionally, the Q_uf_o value of the prepared solid ceramics was also found to be dependent on the sintering temperature and the curve of the Q_uf_o value of the prepared solid ceramics had a consistent variation to that of the density with the sintering temperature. The lowest value of the Q_uf_o value was achieved for the solid 94($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3− 6$CaTiO_3$ceramics at the initial lowest sintering temperature of 1325 °C and raise in the sintering temperature boosted the Q_uf_o value to highest value of 128 x 10^3 GHz which was attained at 1400 °C as shown in figure 1.8. However, further enhancement in the activation temperature caused the curve of the Q_uf_o value towards lower value. This degradation in the Q_uf_o value was attributed to the fall of the apparent density of the solid ceramics at sintering temperature of 1425 °C.

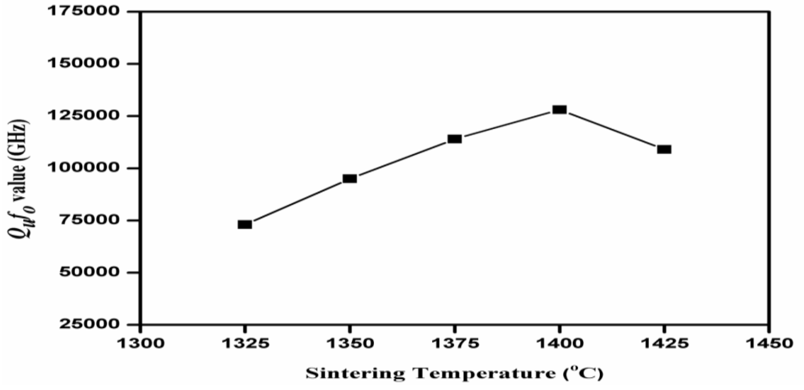

Fig. 1.8: Rise and fall of quality factor value of solid 94($Mg_{0.95}Co_{0.05}$)($Ti_{0.95}Sn_{0.05}$)TiO_3− 6$CaTiO_3$ ceramics as function of sintering temperature.

Temperature Coefficient of Resonant Frequency of The Ceramics

Figure 1.9 demonstrate the dependence of the τ_f value on the sintering temperature of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$. The present research study was conduct for the enhancement of the τ_f value and for this purpose the calcium titanate having high τ_f was added to the solid $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ ceramics. Since, the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ ceramics was initially reported to have high τ_f (− 56 ppm/°C) value which degraded its importance for its use in the practical application. Additives, existence of additional materials formation in the main composition, bulk density are main factors that are accountable for the fluctuation in the τ_f value of any material. In the present study, the τ_f value noted for the solid $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ material containing 6 wt% of calcium titanate as compensator was − 19.5 ppm/°C at sintering temperature of 1325 °C. The reason for this sudden increase of τ_f value from − 56 ppm/°C to − 19.5 ppm/°C is the high positive τ_f (+800 ppm/°C) value which the compensator demonstrates. Moreover, the τ_f also showed fluctuation with the sintering temperature as well. The τ_f value of the prepared ceramics was noted to increase further to – 17.9 ppm/°C with the further enhance in the sintering temperature from 1325 °C to 1350 °C. This enhancement did vanish in the τ_f value at 1350 °C but followed in the same manner with enhancement in the sintering temperature till 1400 °C. However, this trend of enhancement in the τ_f value was vanished after further enhance in the sintering temperature than 1425 °C. Overall the τ_f value of the present prepared solid ceramics fluctuate between the – 19.5 ppm/°C and – 16 ppm/°C.

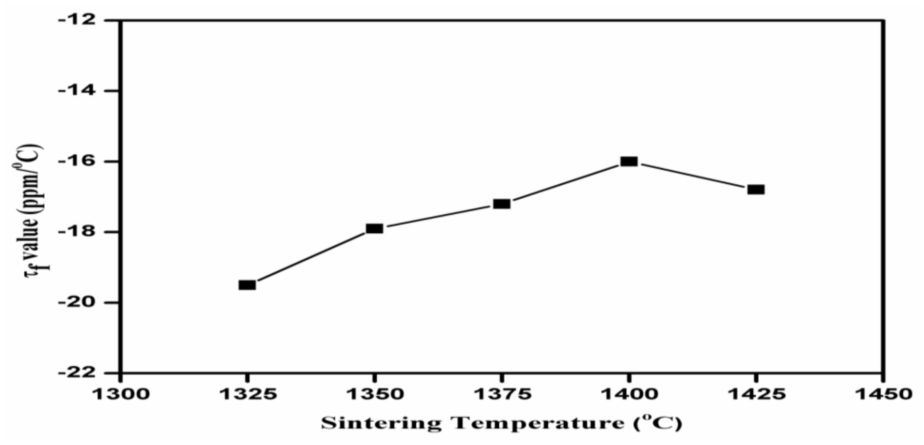

Fig. 1.9: Dependence of the τ_f value on the sintering temperature given to the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TO_3-6CaTiO_3$ceramics.

Conclusion

In the present study a new solid ceramics material was successfully synthesized by using the conventional solid state mixture route. In this mixture method two solid ceramics: $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$having τ_f high negative value of −56 ppm/°C, Q_uf_o value of 288,000 GHz, and ε_r value of 16.6 and $CaTiO_3$ having very high positive τ_f value of 800 ppm/°C, a very low Q_uf_o value of 3600 GHz, and high positive ε_r value of 170 were added with the ratio of 94:6 respectively, after calcining them separately at 1200°C for a stay time of 5 hours. The τ_f of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ ceramics material was enhanced from −56 ppm/°C to −16ppm/°C with the addition of 6 wt% of calcium titanate as τ_f compensator. The addition of the compensator resulted in the formation of two additional phases (i.e., calcium titanate & $MgTi_2O_5$) in the solid $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ ceramics material besides the main phase which were confirmed with the XRD technique. Moreover, the micrograph of the solid $94(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3-6CaTiO_3$ceramics mixture also showed the existence of three different grain which further gave authentication to the XRD results. The experimental density of the solid 94$(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$– 6$CaTiO_3$ceramics were calculated, which showed too much dependence on the sintering temperature. The experimental density was detected to be amplified primarily from 3.71 g/cm^3 noted at sintering temperature of 1325 °C, to 3.86 g/cm^3 which were achieved at 1400 °C but the sintering temperature of 1425 °C was appeared as degrading agent for the density curve. The Q_uf_o value was significantly affected by the addition of compensator and sintering temperature as well. A highest value of 128,000 GHz was noted at sintering temperature of 1400°C. However, further enhance in the deriving temperature degraded the Q_uf_o value. This degradation in the Q_uf_o value was attributed to the decrease in the experimental density which is extrinsic factor and mainly responsible for the fluctuation in the microwave dielectric properties of the solid ceramics. The $□_r$ and $□_f$ were also affected by the addition of compensator. The $□_r$ value was boosted from 16.6 to 19.3 with just 6 wt% addition of calcium titanate and the fact behind this boost was the higher $□_r$ value of the compensator than the host material. The $□_f$ property of the material was too much affected and was enhanced to −16 ppm/°C from −56ppm/°C with the addition of 6 wt% of compensator. After studying the overall behavior of the mixture, it was concluded that such addition of two different solid ceramics materials always cause degradation in some of the microwave dielectric properties, while in some it causes improvement. In the present study, the concluding microwave dielectric properties calculated for the solid $(Mg_{0.95}Co_{0.05})(Ti_{0.95}Sn_{0.05})TiO_3$ ceramics material with the addition of 6 wt% of compensator sintered at 1400 °C were: $□_f$~−16 ppm/°C, $□_r$~ 19.3, and Q_uf_o~ 128,000 GHz.

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