Dielectric studies of single phase Mg_2TiO_4 inverse spinel ceramics via high energy ball milling

R. K. Bhuyan, D. Pamu and B. K. Sahoo

Abstract: In this papaer we have studied the structural and dielectric properties of single phase Mg_2TiO_4 inverse spinel ceramics using X-ray diffraction, Scanning electron microscopy and Dielectric spectroscopy. Polycrystalline Mg_2TiO_4 ceramics is synthesized via high energy ball milling technique and its single phase nature was confirmed by Rigaku high power X- ray diffractometer. The processing parameters and sintering temperatures are optimized and a maximum relative density of 97.75% (of the theoretical density) with uniform microstructure is observed for the Mg_2TiO_4 sample sintered at 1325 ^oC for 3 hours. The dielectric properties were measured in the frequency range of 5 kHz to 1 MHz from room temperature (RT) to 500 ^oC. It is observed that both the dielectric constant and loss tangent (*tan δ*) decreases with frequency and increases with temperature. The value of loss tangent was found to be very small ~ 2.0×10^{-4} in the temperature range of RT to 500 ^oC. The dielectric behavior observed in such type of materials was explained with interfacial polarization predicted by the Maxwell-Wagner model in agreement with Koop's phenomenological theory. Further, the study of ac electrical conductivity is carried out, and which sheds the light on the behavior of the charge carriers under the ac field, their mobility and the mechanism of conduction.

Key words: High energy ball milling, X- ray Diffraction, Microstructure, Dielectric properties, AC conductivity (σ_{ac})

1 INTRODUCTION

In the past decade the development of microwave dielectrics resonators and antennas for the applications in communication systems such as cellular phone, direct broadcasting satellite (DBS), 3G filters and global positioning systems has been rapidly growing [1-4]. However, these dielectric resonators must satisfy three main criteria: a higher permittivity to miniaturize the device, a high quality factor ($Q \times f_o$) for better selectivity and nearly a zero temperature coefficient of resonant frequency (τ_f) to ensure stability of the frequency against temperature changes [3 - 12]. Accordingly, the search on new high Q dielectric materials, such as MgO – TiO_2 binary system, has brought much more attention for high-frequency applications [13, 14]. From which Mg_2TiO_4 ceramic is one of the leading dielectric material with excellent microwave dielectric properties: modest dielectric constant (ε_r) ~ 14, a high-quality factor ($Q \times f_o$) ~150,000 GHz and a negative temperature coefficient of resonant frequency (τ_f) ~ - 50 ppm / ^oC [10, 12, 14].

However, there is a major disadvantage in preparing Mg_2TiO_4 (MTO) ceramics by solid state reaction method that it requires high sintering temperature is about 1450 ^oC. It is difficult to achieve full densification at lower temperatures without additives and these additives may degrade the microwave dielectric properties. Nevertheless, there are several methods used to reduce the sintering temperature of microwave dielectric ceramics such as addition of a low-softening glass or liquid phase sintering aid [15, 16], chemical processing [17] and reduction of initial particle sizes using high energy ball milling [18]. Extensive research revealed that mechanical activation could simplify or accelerate solid state reaction, which normally occurs at high temperature and/ or high pressure [19]. In this present work, MTO nano-ceramics were prepared by high energy ball milling method, which is a convenient method for the synthesis of wide range of nanosized metallic and ceramic powders in an efficient and economical manner [20]. It has many advantages; such as simplicity, relatively inexpensive to produce, applicable to any class of materials [21]. While the most valuable advantage of this technique is that the solid-state reaction is activated via mechanical energy instead of heating energy. Hence, this method skips the calcinations step, which is necessary in the conventional solid- state reaction method and the initial reaction takes place at a temperature close to room temperature in a sealed container [21].

It is well known that MTO is a good candidate for the use of modern communication systems such as filters, oscillators, resonators, dielectric sunstrate, wave guide and antennas. However, from literature review it is found that there is no report on the study of the dielectric properties and ac electrical conductivity of MTO ceramics as a function of frequency (5 kHz to 1 MHz) measured at different temperatures (from room temperature to 500 ^oC), synthesized via high energy ball milling process.

In view of the above importace high energy ball milling technique was used to obtained single phase of MTO ceramics with reduced sintering temperature from 1450 ^oC to 1325 ^oC and characterized by X-ray diffraction, Scanning electron microscopy and dielectric spectroscopy respectively. In particular, the influence of frequency and temperature on the dielectric behavior of MTO ceramics has been discussed.

- *Author : Dr. Ranjan Kumar Bhuyan is currently working as lecturer in Physics Govt. (Autonomous) College Angul, Odisha, India. He did his PhD in Physics from Indian Institute of Technology, Guwahati, Assam, India. PH- 7008907672, E-mail: ranjanphysics.bhuyan8@gmail.com*
- *Co-author: Dr. D. Pamu is currently working as Associate Professore in Physics, Department of Physics, Institute of Technology, Guwahati Guwahati, Assam, India, PH-9678328489,Email: pamu@iitg.ernet.in*
- *Co-author: Dr. Basanta Sahoo is currently working as Assistance Professore in Physics PG Department of Physics, Govt. (Autonomous) College Angul, Odisha, India, Email: basanta@iopb.res.in*

2 EXPERIMENTAL DETAILS

2.1 Materials processing

Mg_2TiO_4 ceramics were synthesized by high energy ball milling technique method from individual high- purity oxide powders MgO and TiO_2 (99.99%) of Sigma Aldrich (St. Louis, MO). The starting materials were mixed according to desired stoichiometry ratio and the powders were ball milled for 35 hours to reach steady state condition (using planetary ball mill (Fritsch, Germany)) with the following parameters: (i) ball-to-powder ratio: 10:1; ball diameter : 8 and 16 mm; ball and vial materials: harden stainless steel; speed: 350 rpm. The high energy ball milling was stopped periodically for every 10 minutes and then resumed for 5 minutes, in order to avoid significant temperature rise. After drying and sieving, the samples were uniaxially pressed into pellets with dimensions of 10 mm in diameter and 4 - 5 mm in thickness under a pressure of 200 MPa. The pellets were sintered in the range of 1250 – 1400 °C for 3 hr in air.

2.2 Characterization techniques

The phase purities of sintered MTO ceramics were examined by recording the XRD patterns using Rigaku high power X-ray diffractometer (RINT 2500 system TTRAX) with Cu-K_α radiation (λ = 1.5406 Å). The surface morphology of sintered MTO ceramics was observed through Scanning Electron Microscopy (Leo 1430 vp). The bulk densities of the sintered samples were calculated by Archimedes method. The dielectric constant and dielectric loss were measured using LCR meter (Wayne Kerr Electronics Pvt. Ltd., Model 1J43100). For the measurement of dielectric constant, silver paint was covered on adjacent sides of pressed cylindrical sintered MTO sample, thereby forming the parallel plate capacitor geometry. A PID temperature controller is used to control the temperature of the heating assembly up to 500 °C. The value of dielectric constant (ε_r) of MTO ceramics was calculated by using following formula:

$$\varepsilon_r = \frac{C \times t}{\varepsilon_0 \times A} \quad (1)$$

where, ε_0 is the permittivity in vacuum which is equal to 8.854×10^{-12} C^2 / N m^2.

3 RESULTS AND DISCUSSION

3.1 XRD Analysis

The XRD patterns of the MTO ceramics sintered at different temperatures for a constant duration of 3 hr are shown in Fig.1. It is observed that all the MTO ceramics exhibit single inverse spinel phase (ICSD-PDF # 06-5792) without the evidence of any additional secondary phase over the entire compositional range. The average crystallite size estimated using Williamson- Hall plot method is found to be 70 nm for the sample sintered at 1325 °C for 3 hr. There are no secondary phases observed from the XRD patterns, suggesting the optimized processing parameters using high energy ball milling techniques.

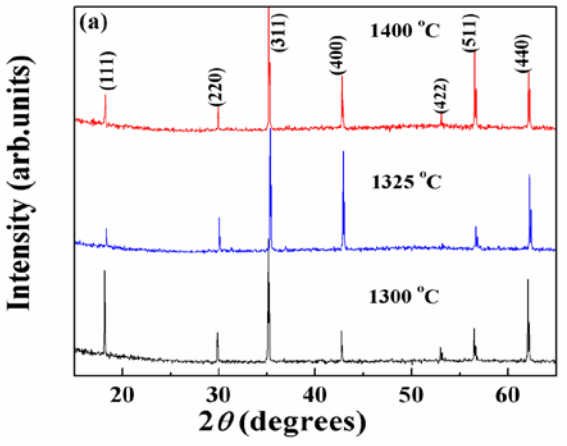


Fig. 1. XRD patterns of the MTO ceramics sintered at different sintering temperatures

3.2 Microstructure and relative density

The SEM micrographs of MTO ceramics sintered at 1325 °C for 3 hr is illustrated in Fig. 2. It is observed that the sample sintered at 1325 °C exhibited uniform grain growth with large grain size compared to other sintered samples with an average grain size of 15-30 μm. To optimize the sintering temperature of MTO ceramics, the variation of relative density as a function of sintering temperature was carried. It was observed that the density for the specimen sintered at 1250 °C was low, but increases with increasing sintering temperature up to 1325 °C and then reduces significantly for 1400 °C. The maximum relative density of 97.75 % was obtained for the sample sintered at 1325 °C for 3 hr. This confirms that the MTO ceramics exhibited highest density at 1325 °C. The increase in the density is mainly due to initial small particle size and uniform grain-growth. On the other hand, the decrease in the density of the sample might be caused by the presence of the pores induced during sintering process.

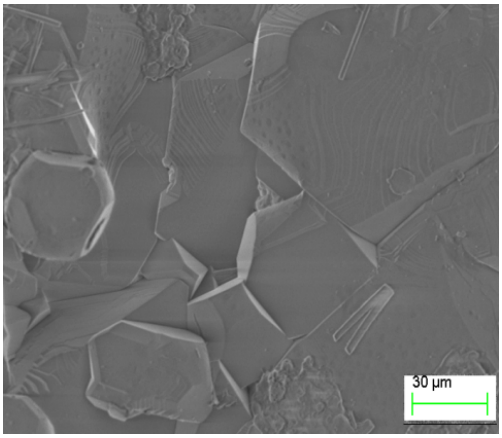
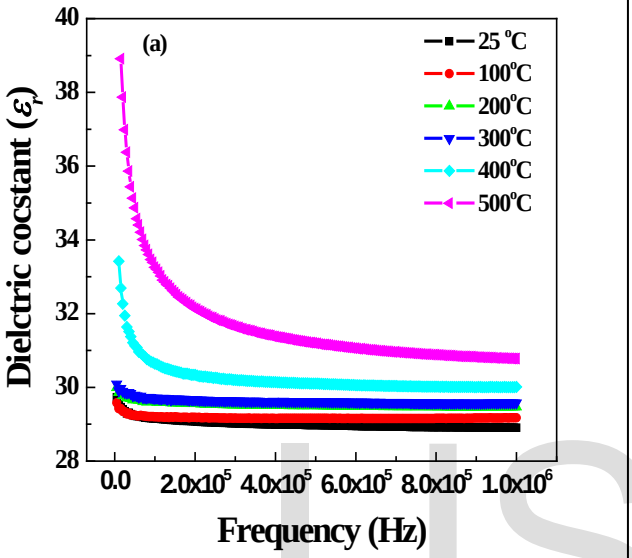


Fig. 2. SEM image of the MTO ceramics sintered 1325 °C

3.2 Dielectric properties

The dielectric properties of MTO ceramics in the frequency range of 5 kHz to 1 MHz from room temperature to 500 °C were measured. Fig. 3 (a,b) illustrates the variation of dielectric constant and dielectric loss as a function of frequency measured at different temperatures for the MTO ceramics sintered at 1325 °C for 3 hr.



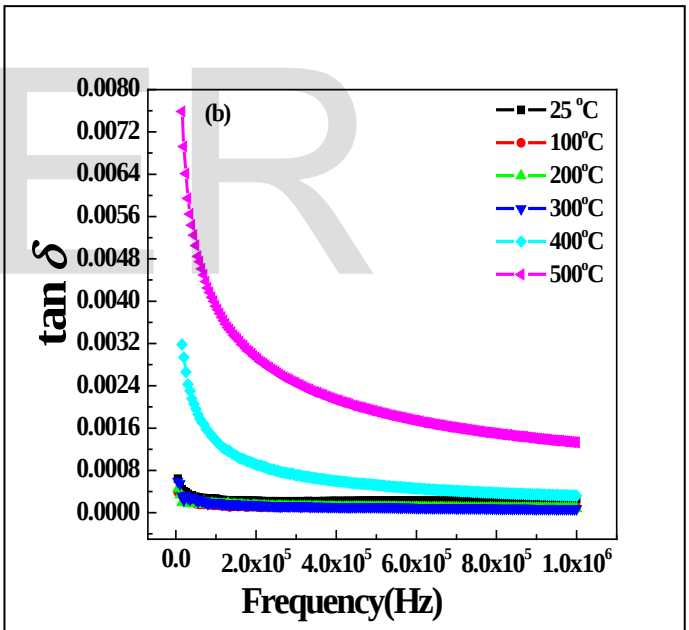
3 (a) Variation of dielectric constant with frequency of MTO ceramics sintered at 1325 °C.

From the plots, it is observed that at lower temperature both the dielectric permittivity (ε_r) and dielectric loss decreases monotonically with increasing frequency up to a certain limiting range (~ 35 kHz) and above that it becomes frequency - independent. This may be due to the inability of electric dipoles to follow the fast variation of the alternating applied electric field. The higher values of ε_r at lower frequencies and at higher temperatures indicate that the polarization in the test materials is larger. This is due to simultaneous presence of all types of polarizations like space charge, dipolar, ionic and electronic, which is found to decrease with the increase in frequency. This also signifies that the resistive grain boundaries become conducting at these temperatures and that grain boundaries are not relaxing even at higher frequency and temperature. The decrease in dielectric permittivity with frequency observed in such type of materials can be explained on the basis of Maxwell-Wagner model [22] in agreement with Koop's phenomenological theory [23].

According to Koop's model, the dielectric materials can be imagined as a heterogeneous structure consisting of high conducting grains with ε_1, σ_1 and thickness d_1 separated by thin layers of poorly conducting grain boundaries with ε_2, σ_2 and thickness d_2. These grain boundaries could be formed during the sintering process either by superficial reduction or oxidation of crystallites in the pores materials due to their direct contact with the firing atmosphere. Koop's assumed that, $y = d_2 / d_1 << 1$, $\sigma_2 << \sigma_1$, $\varepsilon_1 \approx \varepsilon_2$, and the dielectric constant of the sample ε_r, is given by,

$$\varepsilon_r = \varepsilon_1 / y \approx \varepsilon_2 / y \quad (2)$$

Thus the grain boundaries control the behavior of ε_r at lower frequencies, but at higher frequencies only grains are more active in electrical conduction. The thinner the grain boundary layers, the higher the value of ε_r. The dielectric loss shows almost a similar behavior of dielectric constant as seen from Fig. 3 (b). This loss factor curve is considered to be caused by ion migration losses, electron polarization losses and dipolar relaxation losses. At lower temperatures, the monotonic decrease of dielectric loss indicated that at lower temperatures, the relaxation is absent in the materials, i.e., relaxation species are immobile defects and the orientation effects may be associated. Also the decreasing magnitude of ε_r and dielectric loss with increasing frequencies implied that relaxation in the materials is temperature dependent. The dielectric constant and dielectric losses are in the range of 28.1 to 38.9 and 2.0×10^{-4} to 7.5×10^{-3} in the temperature range of room temperature to 500 °C, respectively.



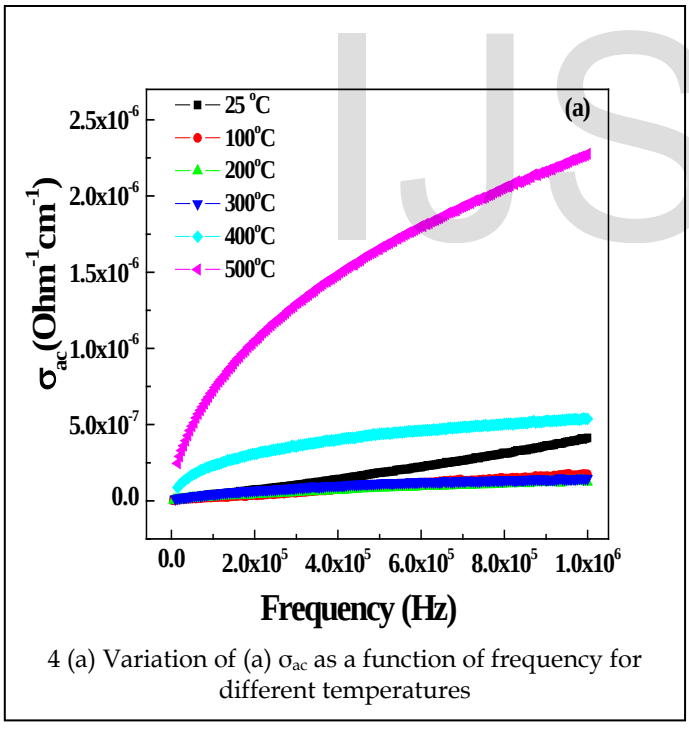
3 (b) Variation of dielectric loss with frequency of MTO ceramics sintered at 1325 °C.

To know the conduction mechanism in MTO samples, the ac conductivity is studied. The dielectric conductivity in ceramics is mainly controlled by the migration of charge species under the action of electric field and the defect-ion complexes, the polarization field, the relaxation etc. The ac conductivity (σ_{ac}) of the MTO ceramics is calculated from the dielectric data by using the relation:

$$\sigma_{ac} = \varepsilon' \varepsilon_o \omega \tan\delta \quad (3)$$

where $\omega = 2\pi f$ (f being the frequency used); ε_o is the permittivity of vacuum (8.85×10^{-12} F/m) and tan δ is the dielectric loss factor. Thus, σ_{ac} is directly related to the dielectric properties of the materials.

The ac conductivity of the system depends on the dielectric properties and sample capacitance. Fig. 4 (a) shows the variation of ac conductivity as a function of frequency at different temperatures. It is observed that the ac conductivity increases not only with the frequency but also with the measurement temperature. Frequency dependent of ac conductivity indicates that conduction occurs due to hoping of charge carriers among the localized states. As the frequency of the applied field increases, the conductive grains become more active and thereby promoting electron hopping between two adjacent sites. At lower frequencies, the grain boundaries are more active and hence the electron-hopping between Ti^{+4} and Ti^{+3} ions is less. But at higher frequencies, the electron-exchange between Ti^{+4} and Ti^{+3} ions might not be able to follow the alternation of the applied ac electric field frequencies and therefore lags behind. Thus the conductivity decreases at higher frequencies. This behavior can be attributed to the relaxation process associated with the domain reorientation, domain wall motion and the dipolar behavior.



4 (a) Variation of (a) σ_{ac} as a function of frequency for different temperatures

Generally, for oxide ceramic materials, the frequency dependence of ac conductivity can be expressed by the empirical formula [24, 25],

$$\sigma(\omega) = A\omega^{s} \quad (4)$$

where s is a dimensionless parameter (power law exponent) which varies between 0 and 1 depending on the temperature, A is a temperature dependent constant having unit of conductivity and ω is the angular frequency at which the conductivity was measured. The exponent s is a measure of the degree of correlation, i.e., s should be zero for random hopping and tends to be one as the correlation of charge carrier increases. In the present work, the value of s was calculated from the relation log (σ_{ac}) versus logω, over the studied range of frequency using eqn. (4), at room temperature and depicted in Fig. 4(b). In the present systems, s values have been found to be 0.91~1, which clearly indicated that there are strong correlations between the charge carriers in the systems, i.e., long range motion of the carriers.

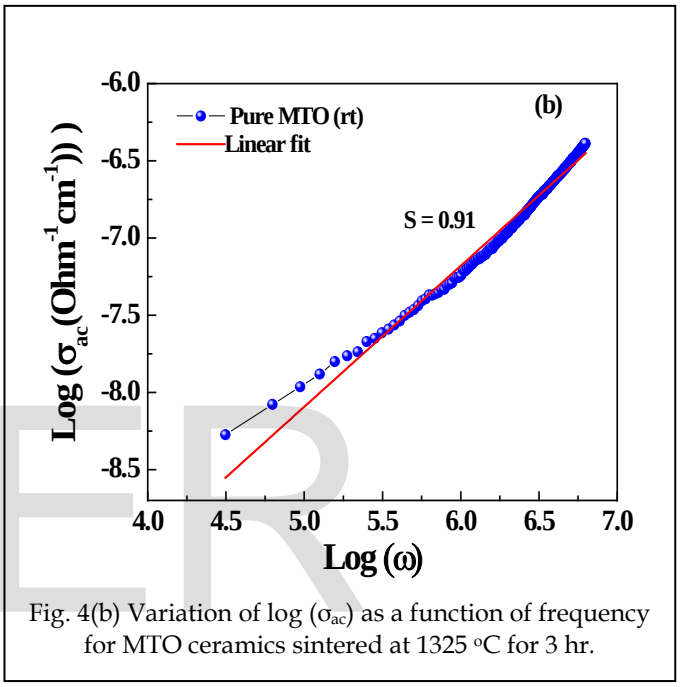


Fig. 4(b) Variation of log (σ_{ac}) as a function of frequency for MTO ceramics sintered at 1325 °C for 3 hr.

Fig.5 illustrates the variation of dielectric constant (ε_r) and loss tangent (tan δ) as a function of temperature of the MTO sample measured at 10^6 Hz. It is observed that both the dielectric constant and tan δ increases linearly with increasing temperature. The observed behavior of the dielectric constant with temperature can be explained as follows: at room temperature, the ions cannot oriented themselves with respect to the direction of the applied field, therefore, they possess a week contribution to the polarization and hence to the dielectric constant. As the temperature increases, the conduction relies on the formation of the lattice defects under the action of thermal excitation. This creates vacancies through which ions motion may proceed under the action of external electric field. Therefore, with increasing temperature the ions gain enough thermal energy to follow the change in the external field quite easily. This enhances their contribution to the polarization leading to an increase in the dielectric constant of the materials. The value of the loss tangent is very small and nearly constant up to 300 °C. At high temperatures, the dielectric losses caused by the dipole mechanism reach their maximum value and the degree of dipole orientation increases. Apart from dipole loss-

es, electrical conduction also increases with increase temperature. These factors would cause the increase in both dielectric constant and dielectric loss of MTO ceramics with increasing temperature.

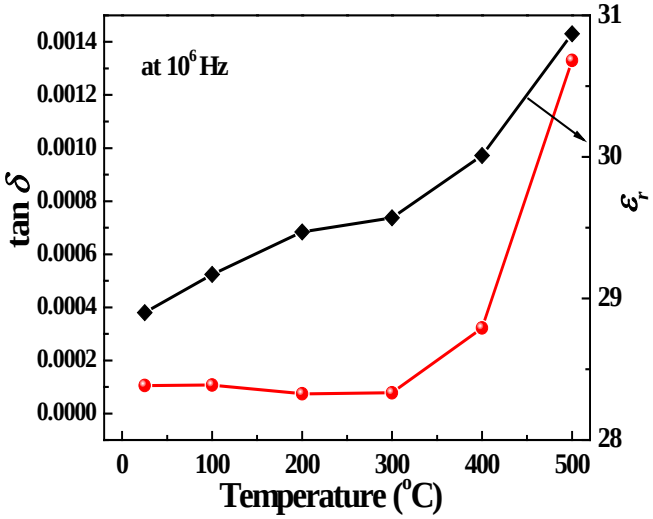


Fig. 5 Variation of dielectric constant and loss tangent (tan δ) as a function of temperature of MTO ceramics, measured at 10^6 MHz

4 CONCLUSIONS

The single phase Mg_2TiO_4 ceramics were successfully prepared by high energy ball milling process. The effects of high energy ball milling on structural, microstructural and the dielectric properties of pure MTO ceramics were studied systematically. The phase purity was confirmed by Rigaku high power X- ray diffractometer. The processing parameters were optimized to reduce the sintering temperature of MTO ceramics from 1400 °C to 1325 °C and a maximum relative density of 97.75 % with uniform microstructure was obtained for the MTO sample sintered at 1325 °C for 3 hr. The dielectric properties were studied as a function of frequency and temperature in the frequency range of 5 kHz to 1 MHz from room temperature to 500 °C respectively and discussed in details. The value of loss tangent was found to be very small ~ 2.0×10^{-4} throughout the whole temperature range. The Mg_2TiO_4 ceramics prepared by high energy ball milling process and having a low value of dielectric loss clearly indicates that this material is suitable for commercial technological applications.

ACKNOWLEDGMENT

The author RKB acknowledges the assistance from DRDO. The author acknowledges Dr. D.Pamu for facilating his laboratory for the measurement of dielectric properties.

REFERENCES

[1] C. L. Huang, J. J. Wang, Y.P. Change (2007), Dielectric properties of low loss (1-x)($Mg_{0.95}Zn_{0.05}$)TiO_3-x$SrTiO_3$ ceramics system at microwave frequency, J. Am., Ceram. Soc., 90: 858-862.

[2] C. L. Huang, S. S. Liu (2008), Low loss microwave dielectrics in the ($Mg_{1-x}Zn_{0x}$)$_2TiO_4$ ceramics, J. Am., Ceram. Soc., 91: 3428-3430.

[3] R. K. Bhuyan, T. Santhosh Kumar, and D. Pamu (2017), Liquid phase effect of Bi_2O_3 additive on densification, microstructure and microwave dielectric propertries of Mg_2TiO_4 ceramics, Ferroelectrics, 516: 173-184

[4] C. L. Huang, J. F. Tseng, (2004), Dielectric characteristics of La(Co1/2O1/2)O3 ceramics system at microwave frequency, Mater. Letts., 58: 3732-3736.

[5] C. L. Huang, C. En. Ho, (2010), Microwave dielectrics in the ($Mg_{1-x}Ni_{0x}$)$_2TiO_4$ ceramics, In. J. Am., Appl. Ceram. Technol., 7: E163-E169.

[6] C. L. Huang, S. S. Liu (2009), Low loss microwave dielectrics in the ($Mg_{1-x}Zn_{0x}$)$_2TiO_4$ ceramics, J. Am., Ceram. Soc., 91: 3428-3430.

[7] R. K. Bhuyan, T. Santhosh Kumar, D. Goswami, A.R. James, A. Perumal and D. Pamu (2013), Enhanced densification and microwave dielectric propertries of Mg_2TiO_4 ceramics added with CeO_2 nanoparticles, Mater, Sci. Eng. B, 178: 471-476.

[8] P. S. Anjana, M. T. Sebastain, M. N. Suma, P. Mohanan, (2008) Low dielectric loss PTFE/CeO_2 ceramic composites for microwave substrate apllication, J. Appl. Ceram. Technol. 5 325-333.

[9] R. J. Cava, (2001) Dielectric materials for applications in microwave communications, J. Mater. Chem., 11: 54-62.

[10] R. K. Bhuyan, T. Santhosh Kumar, A.R. Jamaes and D. Pamu (2013) Structural and microwave dielectric propertries of Mg_2TiO_4 ceramics synthesized by mechanical method, Inter. J. Appl. Ceram. Technol., 10: E18-E24.

[11] Y. B. Chen (2012), Dielectric properties and crystal structure of Mg_2TiO_4 ceramics substituting Mg^{2+} with Zn^{2+} and Co^{2+}; J. Alloys Compd.**513** : 481-486.

[12] A. Belous, O. Ovchar, D. Durilin, M. Valant, M. M. Krzmanc and D. Suvorov, (2007), Microwave composite dielectrics based on magnecium titanates, J. Eur. Ceram. Soc., 27: 2963 – 2966.

[13] B. A. Wechsler, R. B. Von Dreele, *Acta Cryst*., pp. 542-549 (1989).

[14] C. L. Huang, J. Y. Chen (2009), High-Q microwave dielectrics in the ($Mg_{1-x}Co_{0x}$)$_2TiO_4$ ceramics, J. Am., Ceram. Soc., 92: 379-383..

[15] D. Pamu , G. Lakshmi Narayana Rao, K. C. James Raju (2009), Effect of BaO, SrO and MgO addition on microstructure dielectric properties of (Zr0.8Sn0.2)TiO4 Ceramics, J. Alloys. Compd. 475: 745-751.

[16] R. K. Bhuyan, T. Santhosh Kumar, D. Goswami, A.R. Jamaes and D. Pamu (2013), Liquid phase effect of La_2O_3 and V_2O_5 on microwave dielectric propertries of Mg_2TiO_4 ceramics, J. Electroceram, 31: 48-54.

[17] I. R. Abothu, A. V. Prasad Rao and S. Komarneni (1999), Nanocomposite and monophasic synthesis routes to magnesium titanates, Matt. Lett., 38: 186-189.

[18] T. Santhosh Kumar, A. Kumar, A. R. Jamaes and D. Pamu (2011), Enhanced microwave dielectric propertries of $MgTiO_3$ ceramics prepared by mechanochemical method, J. Aus. Ceram. Soc., 42: 44-48.

[19] M. Kamruddin, P. K. Ajikumar, R. Nithya, A. K. Tyagi, B. Raj, (2004), Synthesis of nanocrystalline ceria by thermal decomposition and soft-chemistry methods, Scr. Mater. 50: 417-422.

[20] H. Yang, Y. Hu, A. Tang, S. Jin, G. Qiu, (2004), Synthesis of tin oxide nanoparticles by mechanochemical reaction, J. Alloys. Comp. 363: 271-274.

[21] C. Suryanarayana, *Mechanical Alloying and Milling*, Marcel Dekker,

(2004).

[22] J. Maxwell, Electricity and Magnetic, V-1 section 328, Oxford University Press, London (1873).

[23] C. Koops, (1951) On the dispersion of resistivity and dielectric constant of some semiconductors at audiofrequencies, Phys. Rev., 83: 121-124.

[24] S. R. Elliott, (1987) A.C. conduction in amorphous chalcogenide and pnictide semiconductors, Adv. Phys., 36: 135-217.

[25] A. Ghosh, (1992), Correlated- barrier hopping in semiconducting tellurium molybdate glass, 45: 11318.