Analysis on the influence of ZnO addition on microwave dielectric properties of $\text{Li}_2\text{MgSiO}_4$ ceramics

ALEENA ROSE¹, B MASIN², K ASHOK², H SREEMOOLANADHAN² and T VIJAYAKUMAR^{1,*}

¹Futuristic Materials Research Centre for Planetary Exploration, Department of Physics and Nanotechnology, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur, Kancheepuram 603203, India

²Advanced Materials and Ceramic Division, Vikram Sarabhai Space Center, Thiruvananthapuram 695022, India

*Author for correspondence (vijayakumar.t@vdp.srmuniv.ac.in)

MS received 12 October 2018; accepted 14 February 2019

Abstract. Dielectric ceramics have gained wide attention owing to their applicability in a broad range of domains including a microwave communication system. Silicates are considered as the prospective substrate materials for microwave circuits due to their properties complementing with the requisites of a microwave substrate. Lightweight lithium-based silicate ceramic namely lithium magnesium silicate ($\text{Li}_2\text{MgSiO}_4$, LMS) was prepared by a solid-state reaction method. Zinc oxide (ZnO) was used as an additive to LMS in different weight percentages (0.5, 1.0, 1.5 and 2.0) and LMS-ZnO ceramics were also prepared. The microwave dielectric properties of pure LMS and ZnO-added LMS were measured and the influence of ZnO on LMS was investigated. A dielectric resonance technique was utilized to study the dielectric properties of ceramic samples at 12 GHz. A comparatively higher quality factor of 24,000 GHz was attained by the LMS-ZnO (2 wt%) system with a relative density of 90.2% and <10 dielectric constant of 5.76 making it suitable for substrate applications.

Keywords. Solid-state reaction; silicates; dielectric ceramics; microwave; quality factor.

1. Introduction

Microwaves of the electromagnetic spectrum, residing between radio and infrared waves have been widely explored in the communication field owing to their advantages over radio waves. They can be easily focussed onto narrower beams which allow frequency reuse and relatively higher frequency allocates a wide bandwidth and provides a high-data transmission rate. Since the antenna size is inversely proportional to the transmitted frequency, the antenna size can be reduced. Requisite of a good communication system i.e., transmission of energy and information signals with no interference can be achieved through the use of microwaves. They travel by line of sight propagation and do not follow the Earth's curvature. Large reflections are produced because of their short wavelength. The wavelength similar to the circuit dimensions initiates the use of waveguides and cavity resonators replacing the coaxial transmission lines and lumped-element tuned circuits [1–3]. All these factors increased the use of microwaves in point-to-point telecommunications, radar, remote sensing, satellite communication, tracking applications, etc. Thus, the development of microwave communication field strengthened the exigency for microwave ceramics which possess good dielectric properties, and ability to be incorporated with other materials [4,5]. These highly reliable ceramic systems are utilized for a wide range of applications including antennas, packages, substrates, cell phones, capacitors, filters, resonators, etc. [6–8]. Relative permittivity (ϵ_r) or

dielectric constant, dielectric loss ($\tan \delta$) or quality factor (Q_{uxf}) and temperature coefficient of resonant frequency (τ_f) are the three important parameters which should be optimized for a specific application [9]. Low-loss ceramics with low-dielectric constant values (<10) and near-zero temperature coefficient of the resonant frequency are of great significance owing to their potential to be used as substrate materials in microwave integrated circuits. A substrate material with low ϵ_r and $\tan \delta$ aids the signal transmission by decreasing the noise, propagation delay and signal attenuation, respectively [10–13]. Additionally high Q_{uxf} provides selectivity through discarding the unnecessary signals by its narrow bandwidth [14]. Microwave dielectric ceramics such as silicates, aluminates and phosphates are capable of meeting these requirements [15–17]. Lithium magnesium silicate ($\text{Li}_2\text{MgSiO}_4$), forsterite (Mg_2SiO_4), wollastonite (CaSiO_3), zinc silicate (Zn_2SiO_4), etc. are some of the silicates exhibiting low ϵ_r and $\tan \delta$ which makes them suitable candidates for microwave substrate applications [5,18–20].

Density has a huge impact on the dielectric properties of ceramics. The lack of densification limits the application of silicate compounds in microwave-integrated circuits. The development of a densified ceramic depends on the crystal structure, defects, pore density, fabrication route and the characteristics and concentration of additives and dopants [21]. Porosity, micro-cracks, non-uniform grain growth, grain boundaries, crystal imperfections, etc. reduce the density of the ceramics thereby leading to extrinsic loss [14].

Inclusion of additives or dopants is the widely accepted method to improve the density of a ceramic material. CuO, ZrO₂, TiO₂, MnO₂, ZnO, CaF₂, PbF₂, B₂O₃, etc. are some of the additives used for achieving good densification [22–26]. Among these additives, ZnO is reported to have an immense potential to enhance the microstructural density of dielectric ceramics. Tan *et al* [27] studied the effect of ZnO addition on the densification of forsterite ceramic and concluded that ZnO improved the density and microstructure of forsterite without inducing any chemical changes. Nikzad *et al* [28] achieved a less porous structure and high Quxf of 141,000 GHz for ZnO-added MgTiO₃ at a relatively low-sintering temperature of 1050°C. Research work by Lu *et al* [29] shows that an optimal concentration of ZnO in 0.90Al₂O₃–0.10TiO₂ can reduce the sintering temperature, lessen the number of pores and smoothen the grain size of that ceramics. Muccillo *et al* [30] obtained 94% of the theoretical density for yttrium-doped barium zirconate through ZnO addition. A recent study on ZnO–H₃BO₃ (ZH) addition to ZnO–MgO–TiO₂–CaO (ZMTC) dielectric ceramics revealed the correlation between density, grain shape and dielectric properties of ZMTC and quantity of ZH. In this work, Guo and Zhang [31] achieved a Quxf of 60,000 GHz for 8 wt% of ZH in ZMTC. Besides, ZnO has been used as a sintering aid in LTCC technology for decreasing the sintering temperature below the melting point of electrode materials through liquid phase sintering [32–34]. The aforementioned reports prove the ability of ZnO in promoting the densification and dielectric properties of microwave ceramics. Lithium is a lightweight metal. This type of material is highly appreciated for space applications because lightweight components can reduce the overall weight of satellite. Apart from this, lithium containing ceramic compositions show low-expansion coefficients. But achieving a good quality factor with lithium-based ceramic compounds is difficult. As we have explained earlier, silicates are one of the compounds meeting the requisites for microwave substrate materials. Hence to obtain the synergistic effect, a silicate compound based on lithium is tried in this work.

Here, we have discussed the solid-state synthesis of Li₂MgSiO₄ (LMS) ceramics and impact of ZnO addition on the microwave dielectric properties of the LMS ceramic system. We have analysed the changes occurred in the density and dielectric properties of ceramics for various weight percentages of ZnO.

2. Experimental

LMS and LMS-ZnO ceramic systems were synthesized through a four-step solid-state reaction method. Starting chemicals, Li₂CO₃, MgO and SiO₂ (99.9%, Aldrich Chemical Company), were preheated at 200°C for 1 h in order to remove the moisture content and impurities. Stoichiometrically weighed chemicals were mixed in a roll miller for 5 h by making use of agate balls and de-mineralized (DM) water.

This blend was then dried at 100°C for 2 h. The resulting mix was ground to fine powder in an agate mortar and calcined at 850°C for 4 h. A binder used for green body preparation was 1% polyvinyl alcohol (MW~14,000) solution. Calcined LMS powder was mixed with this binder and cylindrical pellets of about 18 mm diameter and 5.9 mm thickness were made by applying a pressure of 100 MPa in a manual press. Pure LMS was sintered at 1100°C for a duration of 6 h.

LMS-ZnO systems were prepared for four different concentrations of ZnO. Since ZnO was used as an additive, the particular weight percentage (0.5, 1, 1.5 and 2 wt%) of ZnO was added to calcined LMS powder and mixed thoroughly using DM water. Samples were then dried at 100°C for 2 h and ground to fine powder. Third step, green body preparation, was conducted similar to that of pure LMS. The diameter and thickness of LMS-ZnO pellets were 12 and 3 mm, respectively. These ceramic systems were sintered at 1100°C for a duration of 4 h.

Microstructural features of the sintered pellets were analysed by means of a FEI Quanta FEG 200-high resolution scanning electron microscope (HRSEM). Information about the crystal structure and phase purity of the samples was obtained from a CuK α Bruker D8 advance diffractometer. A BRUKER RFS 27: Stand-alone FT-Raman spectrometer was used to capture the Raman spectra of the samples. Density measurements and microwave dielectric properties of sintered ceramics were obtained through the Archimedes method and the dielectric resonance technique (TE01 δ mode) using a scalar network analyser (Aeroflex IFR6823) respectively.

3. Results and discussion

X-ray diffraction (XRD) patterns of LMS and LMS-ZnO ceramic systems are shown in figure 1. All the diffraction patterns shown in the figure are complying with the ICDD

Figure 1. XRD patterns of pure LMS and LMS-ZnO ceramics.

Figure 2. HRSEM of (a) pure LMS, (b) LMS-ZnO (0.5 wt%), (c) LMS-ZnO (1 wt%), (d) LMS-ZnO (1.5 wt%) and (e) LMS-ZnO (2 wt%) ceramic systems.

pattern (024-0636) of LMS having an orthorhombic unit cell as the major phase. The minor secondary phase identified as lithium silicate $\text{Li}_6(\text{Si}_2\text{O}_7)$ has been marked as “*” with very low-intensity reflection. The minor secondary phase, $\text{Li}_6(\text{Si}_2\text{O}_7)$ – ICDD (01-074-0300), is present in both pristine and ZnO-added LMS patterns. It can be seen from figure 1 that addition of ZnO in LMS ceramic did not led to the formation of undesired phases or is not detectable in any of the XRD patterns.

Figure 2a–e shows the HRSEM of pure LMS and LMS-ZnO ceramic systems with 0.5, 1, 1.5 and 2 wt% of ZnO respectively. The microstructure of pure LMS contains more cracks and non-uniform grains in some areas. From figure 2b it is clear that LMS-ZnO (0.5 wt%) shows cracks and trapped intra-granular pores along with large non-uniform grains. These features of microstructures may have a negative influence on the dielectric properties of LMS such as extrinsic loss. In the case of LMS-ZnO (1 wt%), figure 2c, cohesive neck formation is complete but grains of non-uniform sizes and inter-granular pores are there. LMS-ZnO (1.5 wt%) ceramic shown in figure 2d consists of uniform large grains and completely grown cohesive necks compared to previously mentioned samples. The image of LMS-ZnO (2 wt%) captured by HRSEM as shown in figure 2e reveals its better refined microstructure and regular grain size. ZnO addition to LMS ceramics appears to be beneficial in refining the microstructure in terms of grain size and uniformity. Compared to other samples, energy dissipated by this ceramic may be low thus leading to a high-quality factor and low-loss tangent. None of the microstructures showed signs of grain-boundary segregation which might be due to the solubility of ZnO in the LMS system.

Fourier transform (FT)-Raman spectra of LMS and ZnO-added LMS ceramics are shown in figure 3. Sharp and intense peaks are formed at 521 cm^{-1} for LMS and LMS-ZnO ceramic systems. These peaks imply the Si–O–Si bond thus confirming the formation of silicate. Considerable extra peaks are not present in the LMS-ZnO systems. Hence the FT-Raman spectra are in agreement with the corresponding XRD patterns.

Figure 4 shows the relative density and dielectric constant values obtained with the ceramic samples. From the figure, it is clear that density and dielectric constant show identical trends with respect to ZnO addition. Among all the samples pristine LMS achieved the highest relative density of 90.6% with a dielectric constant of 5.73. But, this ceramic needed more duration for sintering (6 h at 1100°C). Reducing the duration of sintering to 4 h in LMS ceramics, 0.5 and 1 wt% ZnO addition resulted only in 85.8 and 88.2% of theoretical density. The highest relative density of pure LMS can be attributed to the way of mixing and sintering duration employed for LMS ceramics. Pure LMS was mixed through roll milling whereas ZnO was added to pure LMS through mortar grinding. But, addition of ZnO helped in the complete grain growth and the formation of uniform grain boundaries which is evident from the SEM results. Roll milling,

Figure 3. FT-Raman spectra of pure LMS and LMS-ZnO ceramics.

Figure 4. Relative density and dielectric constant values of pure LMS and LMS-ZnO ceramics.

which is an efficient way of mixing the starting materials in a stoichiometric ratio, may be applied to increase the density of LMS-ZnO ceramics. The microstructures corresponding to these ceramics in figure 2 showed porosity and incomplete densification. The neck-formation has been quite good but without sufficient grain coarsening. Because of this poor densification, relative permittivity of 0.5 and 1 wt% ZnO-added LMS ceramics exhibited relatively lower dielectric constants of 5.41 and 5.63, respectively compared to the pristine sample. But, addition of ZnO 1.5 and 2 wt% in LMS ceramics achieved nearly the same density (90.2% relative density) as

that of pristine samples heated for 6 h. It can be seen in figure 4 that the dielectric constant values of 1.5 and 2 wt%-added LMS ceramics showed identical values with that of pristine ceramics.

Figure 5 displays the microwave dielectric Quxf of LMS and LMS-ZnO ceramics measured by a TE₀₁ δ mode dielectric resonance technique at 12 GHz. The density and porosity of ceramics are really important in the quality factor of ceramics. Since the quality factor is the inverse of dielectric loss, the loss contributed by porosity, secondary phases or segregation and other microstructural defects decrease this parameter. Quxf initially decreases with ZnO addition like bulk density and then increases. Pristine LMS and LMS with ZnO (1 wt%) show almost similar Quxf values. With further ZnO addition, the Quxf increases reaching the highest (24,000 GHz) for 2% ZnO addition to LMS ceramic. From the HRSEM images (figure 2a–d) it is obvious that the LMS-ZnO (2 wt%) sample contained homogenous grain growth and cohesive neck formations with less porosity. This fine microstructural feature has led to the highest quality factor. While comparing figures 2, 4 and 5, it is comprehensible that the density and microwave dielectric properties of LMS-ZnO (0.5 wt%) were negatively affected by the presence of irregular grains, pores and micro-cracks leading to the lowest Quxf value. Thus, addition of 1.5 and 2 wt% of ZnO enhanced the microwave dielectric properties of LMS. The appearance of pores and

cracks in the 0.5 and 1 wt% LMS-ZnO samples deteriorated microstructural density thereby reducing the quality factor and dielectric constant values. Since the dielectric properties of LMS are improved for the higher concentrations of ZnO, this additive can be used in various concentrations with LMS for achieving a high quality factor. The presence of impurities in raw materials and contagion in the course of milling can cause less quality factor. Density of the final product can be enhanced by increasing the mixing time. An optimized milling duration can achieve uniform grain distribution thereby providing a dense microstructure. The right balance of these factors should be maintained to obtain a better quality ceramics. Variation in the dielectric constant is caused by the strength of bonding where increased bond strength lessens the relative permittivity value. Covalently bonded elements inside the LMS ceramic are the reason for decreased dielectric constants. The microwave dielectric properties of the LMS and LMS-ZnO ceramic systems prove that these are suitable candidates for substrate applications. Table 1 shows the density, relative density, dielectric constant, tangent loss and quality factor of the LMS and LMS-ZnO ceramic systems. Variation in the microwave dielectric properties of LMS upon the addition of different compounds is shown in figure 6 [35]. LMS with ZnO exhibits the lowest dielectric loss value and a below 10 dielectric constant value which indicates its capability to be used as an additive.

Figure 5. Quality factor of pure LMS and LMS-ZnO ceramics.

Figure 6. Comparison chart on the dielectric properties of LMS ceramics with different additives.

Table 1. Relative density and microwave dielectric properties of LMS and LMS-ZnO ceramics.

Sl. No.	ZnO in LMS (wt%)	Relative density (%)	Dielectric constant (ϵ_r)	Quality factor (Quxf) GHz
1	0.0	90.6	5.73	20,000
2	0.5	85.8	5.41	15,000
3	1.0	88.2	5.63	20,000
4	1.5	90.2	5.8	21,000
5	2.0	90.2	5.76	24,000

4. Conclusion

An effect of ZnO addition on the microwave dielectric properties of LMS was examined. LMS-ZnO with 1.5 and 2 wt% ZnO showed a relatively higher quality factor among all ceramic systems. Pure LMS ceramic achieved the highest relative density of 90.6% and a Q_{uxf} value higher than that of the 0.5 wt% LMS-ZnO system due to the long duration of sintering temperature. The quality factor improved with the increasing weight percentage of ZnO in LMS. Also, relative permittivity exhibited by all the ceramic systems was <10 . ZnO as an additive, thus, enhances the quality factor of LMS. Hence, LMS-ZnO ceramics can be investigated for higher concentrations of ZnO with the aim of obtaining the enhanced microwave dielectric properties apposite for substrate applications. LMS-ZnO (2 wt%) ceramic showed the good dielectric properties of $Q_{\text{uxf}} = 24,000$ GHz and $\epsilon_r = 5.76$ at 12 GHz while it acquired 90.2% of theoretical density. ZnO-addition is beneficial in LMS ceramics in reducing the sintering duration and achieving 20% or more quality factor.

Acknowledgements

The authors express their thanks to SRM University, Chennai, India, Advanced Materials and Ceramic Division, Vikram Sarabhai Space Centre, Trivandrum, India, and Department of Science and Technology (DST), SAIF-IIT Madras, India, for providing assistance to complete this research work.

References

- [1] Pozar D M 2009 *Microwave engineering* (Hoboken, New Jersey, United States: Wiley)
- [2] Sorrentino R and Bianchi G 2010 *Microwave and RF engineering* (Hoboken, New Jersey, United States: Wiley)
- [3] Jones G A, Lyster D H and Osenkowsky T G 2013 *National association of broadcasters engineering handbook: NAB engineering handbook* (Abingdon, United Kingdom: Taylor & Francis)
- [4] George S, Sajith V, Sebastian M T, Raman S and Mohanan P 2011 *J. Adv. Dielectr.* **1** 209
- [5] George S, Anjana P S, Deepu V N, Mohanan P and Sebastian M T 2009 *J. Am. Ceram. Soc.* **92** 1244
- [6] Reaney I M and Iddles D 2006 *J. Am. Ceram. Soc.* **89** 2063
- [7] Sebastian M T 2010 *Dielectric materials for wireless communication* (Amsterdam, The Netherlands: Elsevier)
- [8] Singh N, Kumar P and Rai R 2011 *Adv. Mater. Lett.* **2** 200
- [9] Sunny A, Lazer K A, Manu K M, Surendran K P and Sebastian M T 2013 *J. Alloys Compd.* **552** 83
- [10] George S and Sebastian M T 2010 *J. Eur. Ceram. Soc.* **30** 2585
- [11] George S and Sebastian M T 2010 *J. Am. Ceram. Soc.* **93** 2164
- [12] Kolodiaznyy T 2012 *J. Eur. Ceram. Soc.* **32** 4305
- [13] Chen X, Zhang W, Bai S and Du Y 2013 *Ceram. Int.* **39** 6355
- [14] Muhammad R, Iqbal Y, Rambo C R and Khan H 2014 *Int. J. Mater. Res.* **105** 431
- [15] Thomas D, Rethika K and Sebastian M T 2012 *J. Mater. Sci.: Mater. Electron.* **23** 1268
- [16] Hu Y, Wei D, Fu Q, Zhao J and Zhou D 2012 *J. Eur. Ceram. Soc.* **32** 521
- [17] Sasikala T, Suma M, Mohanan P, Pavithran C and Sebastian M T 2008 *J. Alloys Compd.* **461** 555
- [18] Nguyen N H, Lim J B, Nahm S, Paik J H and Kim J H 2007 *J. Am. Ceram. Soc.* **90** 3127
- [19] Wang H, Zhang Q, Yang H and Sun H 2008 *Ceram. Int.* **34** 1405
- [20] Song K and Chen X 2008 *Mater. Lett.* **62** 520
- [21] Sebastian M T and Jantunen H 2008 *Int. Mater. Rev.* **53** 57
- [22] Li J, Tian Z, Yao L, Ran S and Fan C 2017 *Ceram. Int.* **43** 15793
- [23] Liu C, Zhang H, Wang G, Zhou T, Su H, Jia L *et al* 2017 *Mater. Res. Bull.* **93** 16
- [24] Redozubov S, Kartenko N, Gaidamaka I and Nenasheva E 2016 *Inorg. Mater.* **52** 1166
- [25] Zhang P, Wang T, Xia W and Li L 2012 *J. Alloys Compd.* **535** 1
- [26] Agathopoulos S 2012 *J. Ceram. Soc. Jpn.* **120** 233
- [27] Tan C, Tan Y, Ramesh S and Yap B 2017 *IOP Conf. Series: Mater. Sci. Eng.* **206** 012051
- [28] Nikzad L, Majidian H, Ghofrani S and Ebadzadeh T 2018 *Int. J. Appl. Ceram. Technol.* **15** 569
- [29] Lu X, Huang B, Chen T, Fu Z, Wang Z, Wang L *et al* 2016 *J. Mater. Sci.: Mater. Electron.* **27** 2687
- [30] Muccillo R, Muccillo E, Andrade T and Oliveira O 2017 *J. Therm. Anal. Calorimetry* **130** 1791
- [31] Guo Y and Zhang Y 2017 *J. Mater. Sci.: Mater. Electron.* **28** 7248
- [32] Xie F, Jia L, Xu F, Li J, Liao Y, Li D *et al* 2018 *J. Mater. Sci.: Mater. Electron.* **29** 5885
- [33] Weng Z, Guan R and Xiong Z 2017 *J. Alloys Compd.* **695** 3517
- [34] Li L, Li J, Zhang N, Cai Z, Zhang B and Luo W 2017 *J. Mater. Sci.: Mater. Electron.* **28** 9763
- [35] Rose A, Masin B, Sreemoolanadhan H, Ashok K and Vijayakumar T 2018 *Appl. Surf. Sci.* **449** 96