Structural Characterization of $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) Perovskite for Mobile communications

Kouros Khamoushi, Vojislav Mitić, Jelena Manojlović, Vesna Paunović, *Member, IEEE*, Goran Lazović

***Abstract*—The phase group and structure properties of $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) ceramics, prepared via the mixed oxide route, were examined in this research. A single-phase $La(Mg_{1/2}Ti_{1/2})O_3$ ceramic were produced at different sintering temperature from 1250ºC to 1675ºC. The heating rate was 25 ° C to the sintering temperature and the cooling rate from 2 ° C per minute to room temperature. The XRD analysis determined that LMT ceramics have a cubic crystal structure with a lattice parameter a = 0.392 nm. The theoretical density of this ceramics is 6.0846 g/cm3. These materials must be sintered from 1550-1675°C to achieve a sintering density of about 99% of theoretical density. At a temperature lower than 1500°C a density was 93% of theoretical density. The temperature coefficient of resonant frequency for LMT was -72 ppm/ºC, and the Quality factor was 34000 at a frequency of 8.07 GHz.**

Key words- Microstructure: Grain growth; single phase $La(Mg_{1/2}Ti_{1/2})O_3$; Lanthanum magnesium titanium oxide.

1. INTRODUCTION

Ceramic components made of dielectric material are important for the operation of filters and oscillators in several microwave systems, such as military radar systems, mobile communications, and satellite TV receivers. Perovskites have a cubic structure with the general formula ABO3, and many are based on BaTiO3. If barium ions are located at the corner of the cube, oxygen is located at face-centered sites, and titanium ions occupy the body-centered sites. Distortion of this sort of compound produces an electrical signal, permitting BaTiO3 to serve as a transducer [1]. The size of the ions has an important share in the stability of the crystal structure, and low distortions can result in lower symmetry and drastically change the property of the compound [2]. An important class of perovskites is multiferroic, which simultaneously shows ferromagnetic, ferroelectric, and ferroelastic parameters in the same segment. Another advantage of perovskite compound is in medical imaging which they can be ten times more sensitive when is used for X-ray detector [3].

In microwave communications, a dielectric resonator filter is used to discriminate between wanted and unwanted signal frequencies in the transmitted and received signal. When the wanted frequency is extracted and detected, it is necessary to maintain a strong signal nevertheless. For clarity, it is also critical that seasonal temperature changes do not affect the expected signal frequencies, and resonator materials for practical application should have reliable properties. A high relative dielectric constant is needed so that the materials can be miniaturized, and a high-quality factor (Q) for improved selectivity. Low-temperature variation of the material's resonant frequency is also required so that the microwave circuits remain stable. Everything from the electromagnetic properties to the microstructure of the material is important for the result.

The gain to reduce the size, load, and expense of microelectronic tools rules for tuning τ_f in multipart perovskites have already been created, accompanied by the piezoelectric materials the most leading material is $Pb(Zr_x Ti_{1-x})$ or PZT which have much application in ultrasound transducer ceramics which used also as capacitor [4,5] according to the work [6] that τ_ε in Ba- and Sr-based complex perovskites are profoundly connected to the start and degree of octahedral tilting. Moreover, it can be tuned through ±300 MK^{-1} without significantly adjusting Q or dielectric constant (ε_r) by manipulating the perovskite tolerance factor, *t*,

$$t = \frac{R_A + R_O}{\sqrt{2}\,(R_B + R_O)} \qquad (1)$$

from 1.01 - 0.93, where R_A, R_B, and R_O are the radii of the ions in the perovskite (ABO_3) structure. Reducing *t* results in the initiation of octahedral tilt modifications. The link between τ_ε and τ_f is:

$$\tau_f = -\left(\tau_\varepsilon / 2 + \alpha_L\right) \qquad (2)$$

Kouros Khamoushi - Natural Science, Tampere University, P.O. Box 1001 FI-33014Tampere, 33720/ Finland, (Email:kouros.khamoushi@tuni.fi).

Vojislav Mitić - University of Niš, Faculty of Electronic Engineering,, Aleksandera Medvedova 14 Niš 18000 Serbia**,** **(**Email: vmitic.d2480@gmail.com**).**

Jelena Manojlović- University of Niš, Faculty of Mechanical Engineering,, Aleksandera Medvedova 14 Niš 18000 Serbia, **(**Email: jmanojlo@gmail.com)

Vesna Paunović – University of Niš, Faculty of Electronic Engineering, Aleksandra Medvedeva 14, 18000 Niš, Srbija (email: vesna.paunovic@elfak.ni.ac.rs).

Goran Lazović- University of Belgrade, Faculty of Mechanical Engineering, Serbia, (email: goran.lazovic@gmail.com)

where α_L is the coefficient of linear thermal expansion (≈10 MK^{-1} for perovskites).

$La(Mg_{1/2}Ti_{1/2})O_3$ is a perovskite formed in the pseudocubic system, although the exact crystal structure has not been fully elucidated. Its tolerance factor is t = 0.95, which, approves to the work [7], reveals the existence of both in-phase and anti-phase tilting of oxygen octahedra. The impacts of this tilting have been detected by XRD in the form of ½(111) ordering at 1600ºC sample.

Superlattice reflections corresponding to anti-phase and in-phase tilting, respectively. Systematic cation displacement was also detected by the presence of ½(210) and ½(111) reflections were observed and attributed to the expansion of the unit cell caused by the B-site cation changes. It is possible by the present tilts to reveal two possible orthorhombic space groups (Pbmn or $P2_1/n$) for the structure, but Walsenburg photographs or TEM work would be required to establish the structure.

Structurally, tilting of octahedra has similar effects as cation ordering in 1:1 type complex perovskites. Both result in expanding unit cells [8] even though cation order also reduces the space available in which the A-site cation types can rattle, it depends on the radii size of rear earth elements used in the compound. In this study, the structural characteristic of $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) in various sintering temperatures for the application of mobile phones and telecommunications was investigated.

2. Experimental Procedure

In this work, conventional mixed oxide powder processing techniques were used for the preparation of samples. A detailed description of the laboratory procedure for sample preparation is given in references [9] and [10]. Starting materials included La_2O_3 (99.9% Meldform Rare Earths, U.K), TiO (99.8% Alfa Aesar, U.K.), and $(MgCO_3)_4Mg(OH)_25H_2O$ (99% Aldrich Chemical Company, Inc, USA). La_2O_3, the rare-earth oxide, was first purposely hydrated in distilled water to form $La(OH)_3$. These hydrates were then used in the subsequent processing method, which involved milling stoichiometric quantities of powders together in a porcelain mill pot partly filled with ZrO_2 media and distilled water for four hours.

A small amount (1wt%) of Dispex A40 (Allied Colloids, Bradford, U.K.) was added as a deflocculant. The slurries were then dried overnight at 80°C. Dried powders were subsequently granulated with a mortar and pestle and sieved to under 250 µm. Calcination was achieved using a two-stage process. First, the powder was heated to 650 ºC for 2 hours in an open Al_2O_3 crucible to ensure dihydroxylation of the $La(OH)_3$. The completion of the dihydroxylation reaction was monitored by measuring the weight loss at this stage of the process. Second, this same powder was combined by hand, a lid was placed over the crucible, and it was re-heated to 1400ºC for 2 hours. Afterward, the powder was re-milled for a further four hours with 2wt% PEG 1500 (Whyte Chemicals, London) being added in an aqueous solution 5-15 min before completion. These slurries were then dried and granulated as above and subsequently pressed (125 MPa) into cylindrical pellets 10 mm in diameter and 3 mm thick. Sintering was conducted in closed alumina boats for 6 hours at temperatures ranging from 1125°C to 1675°C. Pellets were weighed up before and after sintering to quantify the degree of deficiency. Dense and homogeneous ceramic powder of lanthanum magnesium titanium oxide was obtained after pressing powder 125 MPa and sintering at 1600°C for 6 hours.

Phase groupings were verified by scanning electron microscopy (JSM 6300, Jeol, Tokyo) and x-ray diffraction (D50000, Siemens, Germany), using CuKa radiation. Some samples underwent thinning by ion milling (model 600, Gatan, California, USA) for observation in the transmission electron microscope (JEM 2010, Jeol, Tokyo).

3. Results and Discussion

Figure 1 shows the change in density of La $(Mg_{1/2}Ti_{1/2})O_3$ ceramics as a function of sintering temperature. The density of LMT ceramics increased with increasing sintering temperature and reached (87% TD) at 1250°C. Until the sintering temperature of 1300°C, the densities do not change, and then increases to (98% TD) at 1500°C. At this temperature, high-quality, high-density material is obtained.

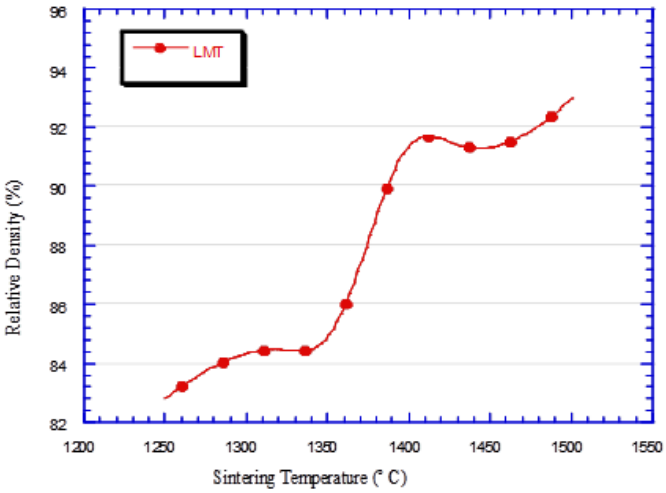

Fig. 1. Relative density of LMT samples in function of sintering temperature (Tsin=1250-1500 ºC).

XRD patterns of LMT samples, sintered at 1400-1675ºC temperature, were shown in Fig 2. Eleven samples were selected, and starting sample was sintered at 1400 ºC for 6 hours and this sintering process continued for each individual sample by increasing 25 ºC to the previous temperature. This successive test continued for every sample and ended at 1675ºC. All the samples show perovskite crystal structure. Peaks from 1400-1675ºC match the LMT structure. All the peaks match PDF card numbers 49-242. Crystallography

search match indicates that crystal structures of samples are cubic with a space group of Pa3.

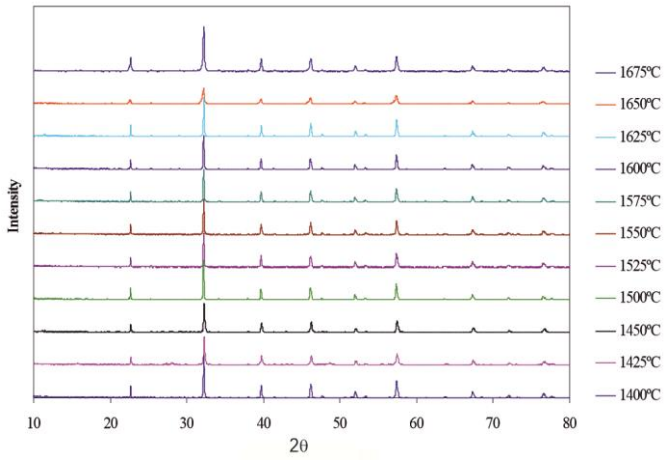

Fig. 2. X-ray diffraction (XRD) of LMT for sintering temperature of 1400-1675ºC.

The SEM image of $La(Mg_{1/2}Ti_{1/2})O_3$ is shown in Figure 3. The image shows an LMT sample sintered at 1650°C. As can be seen from Figure 3, the sample is a single-phase high-dense ceramics. The material with the second phase must show a different contrast. The background scattered image of these samples showed no differences. If the samples show two different colors in contrast, then the investigated material is not single-phase and has impurities. However, several samples of LMT were tested, and all results show pure and very dense LMT material. Also, these samples are characterized by polygonal grains the size ranging from 1 to 6μm.

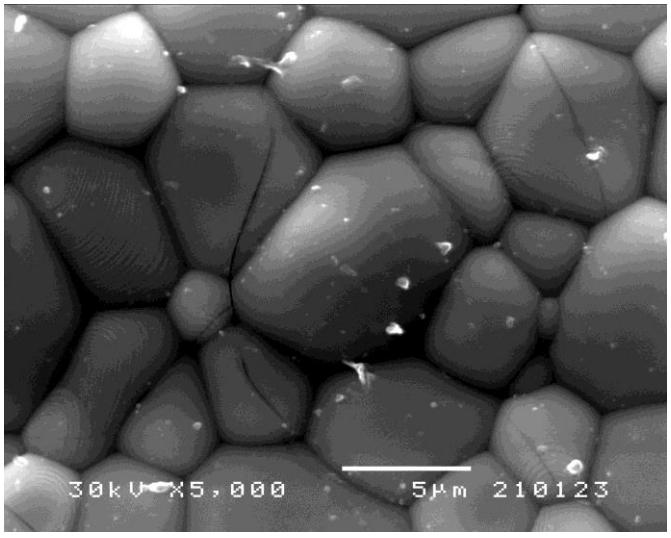

Fig. 3. SEM microphotography of LMT ceramics, sintered at 1650 °C, beam direction [111].

3.1. STRUCTURE OF $La(Mg_{1/2}Ti_{1/2})O_3$

The X-ray pattern for LMT powder shown in figure 4. It is indexed according to the Magnesium Lanthanum Titanium Oxide PDF card number 49-242 with single phase cubic crystal structure with $a \approx 0.3.92$ nm. XRD of sample powder did not show any broadening or splitting of cubic peaks. All the XRD taken from sample of calcined as well as the sintered pellets were similar.

Nevertheless, to avoid the uncertainty for the definition of the exact crystal structure and space group of LMT samples, high resolution transmission electron microscopy and Rietveld refinement by using GSAS should be performed, this work is under consideration for future.

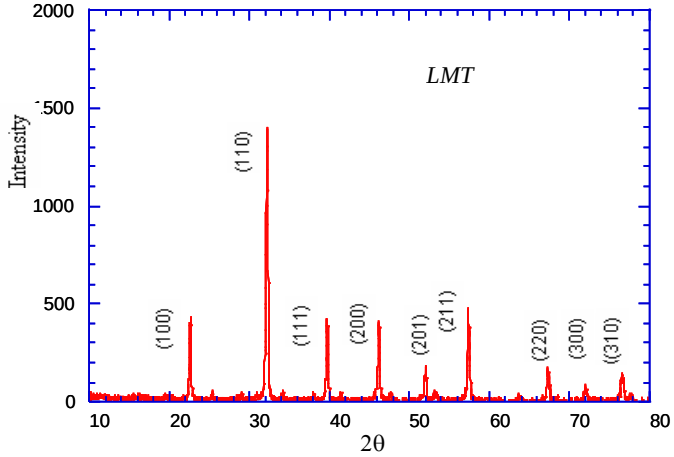

Fig. 4. X-ray diffraction pattern of $La(Mg_{1/2}Ti_{1/2})O_3$ powder after sintered at 1600°C. All the peaks have been indexed according to PDF card numbers 49-242

The temperature coefficient of the microwave resonant frequency (τ_f) and the quality factor (Q) at the resonant frequency were made from the dielectric characteristics.

The results of Q × f measurements illustrate that LMT ceramics have quality factors Q × f = 34,000 at frequency 8.07 GHz. The temperature coefficient of the resonant frequency of LMT is τ_f= -72 ppm/ ºC.

4. CONCLUSIONS AND FUTURE WORK

In this paper the structure characteristics of $La(Mg_{1/2}Ti_{1/2})O_3$ were explored. LMT has lattice parameter a = 0.392 nm and it shows a cubic crystal structure. The theoretical density is 6.0846 g/cm^3. This material can be sintered from 1550-1675 ºC to achieve sintering density of about 99% (1550ºC and 1600ºC). At lower temperature the density was under 97% that of theoretical density. The temperature coefficient of resonant frequency for LMT was -72 ppm/ ºC. The quality factor for LMT was 34000 where saturated at frequency 8.07 GHz. Clearly these materials show a good potential as filters for mobile microwave telecommunications.

Acknowledgements:

This work has been supported by Queen Mary University of London, UK, Tampere University of Technology, Finland, and the Ministry of Education, Science and Technological Development of the Republic of Serbia (Ev. No. 451-03-9 / 2021-14 / 200102).

REFERENCES

[1] K. A. Muller and T. W. Kool, properties of Perovskite and other oxide, world Scientific Publishing, Singapore (2010).

[2] H. Tanaka, H. Tabata, K. Ota, T. Kawai, "Molecular dynamics prediction of structural anomalies in ferroelectric and dielectric $BaTiO_3$-$SrTiO_3$-$CaTiO_3$ solid solutions" Physical ReviewVol.53, no 21, p. 14112-14113, 6th Ed. (1996).

[3] YC Kim, KH Kim, DY Son, DN Jeong, JY Seo, YS Choi "Printable organometallic perovskite enables large-area, low-dose X-ray imaging,", Nature, 550, 87 (2017).

[4] C. Rossel1, M. Sousa1, S. Abel1, D. Caimi, A. Suhm , J. Abergel,G. Le Rhun, and E. Defay. Defay. "Temperature dependence of the transverse piezoelectric coefficient of thin films and aging effects" Journal of Applied Physics, 115, 034105 (2014).

[5] Yingfen Wei, Pavan Nukala, Mart Salverda, Sylvia Matzen, Hong Jian Zhao, Jamo Momand,Arnoud S. Everhardt, Guillaume Agnus, Graeme R. Blake, Philippe Lecoeur, Bart J. Kooi, Jorge Íñiguez, Brahim Dkhil, "A rhombohedral ferroelectric phase in epitaxially strained Hf0.5 Zr0.5O2 thin film "Journal of Nature materials (2018) 17,pages 1095–1100 (2018).

[6] Kouros. Khamoushi, Vojislav. V. Mitic "Comparison between crystal structire and dielectric properties $Nd(Mg_{1/2}Ti_{1/2})O_3$ (NMT) and $Nd(Zn_{1/2}Ti_{1/2})O_3$ (NZT)," In process accepted on 11.5.2021 Journal of Modern Physics Letters B, (2021).

[7] D.Y.Lee S.J.Yoon, J.H.Yeo, S.Nahm,J.H.Paik, K.C.Whang, and B.G.Ahn,"Crystal structure and Microwave Dielectric properties of La(Mg½ Ti½)O3 ceramics," Journal of Materials Science Letter, vol.19 pp131-134(2000).

[8] M.P Seabra, A N Salak, M Avdeev and M Ferreira., "Structure and dielectric characterization of the $La(Mg½Ti½)O_3$-$Nd(Mg½ Ti½)O_3$ system," Journal of Physics Condensed Matter,", 15, (2003).

[9] R. Ubic, K. Khamoushi, Hu, and Isaac Abrahams, "Structure and properties of La(Mg0.5 Ti0.5)O3," Journal of European Ceramic Society, No.26, 1787-1790 (2005).

[10] R. Ubic, K. Khamoushi, D. Iddles, T. Price, "Processing and dielectric properties of $La(Mg_{0.5}Ti_{0.5})O_3$ and Nd $Mg_{0.5}Ti_{0.5})O_3$," Ceramic transaction, 167, 21-3, (2004)