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Structure determination and microwave dielectric properties of $La(MgSn)_{0.5}O_3$ ceramics

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Abstract

$La(MgSn)_{0.5}O_3$ (LMS) has been prepared by solid-state reaction method. A single perovskite phase with super lattice reflections corresponding to octahedral tilting, A-site cation displacement and 1:1 B-site ordering was observed in X-ray diffraction pattern. The Rietveld analysis was carried out with the initial model obtained from Structure Prediction and Diagnostics Software (SPuDS). The structure is determined to be monoclinic with space group $P2_1/n$ corresponding to $a^-a^-c^+$ tilting system. Long range ordering parameter (LRO) between Mg^{2+} and Sn^{4+} ions is calculated to be 89%. Dielectric characterization at microwave frequencies is also carried out. The dielectric constant (ε_r), product of quality factor and resonant frequency (Q.f) and temperature coefficient of resonant frequency (τ_f) of the sample sintered at 1600 °C are 20.1, 63,000 (GHz) and −78 (ppm/°C), respectively.

Keywords: $La(MgSn)_{0.5}O_3$; Powders-solid state reaction; X-ray methods; Dielectric properties

1. Introduction

Next-generation designs, spectral crowding and commercial realities are creating continuous need to reduce the dielectric loss and lower the cost of ceramic resonators and filters.[1] Recently, Lanthanum based 1:1 B-site ordered complex perovskites with $a^-a^-c^+$ Glazer tilt system and monoclinic $P2_1/n$ space group were investigated for the potential application as dielectric resonators.[2–5] Study of these materials is interesting as 1:1 ordering is easily attainable compared to 1:2 ordering[6] and does not contain materials like tantalum that are expensive. Dielectric constants (ε_r) of these compounds were reported to be in the range 28–34, Q.f values were in the range of 36,000–63,000 and temperature coefficients of resonant frequency (τ_f) were in the range of −70 to −79.

Solid compositions of $La(MgTi)_{0.5}O_3$ (LMT) and $La(ZnTi)_{0.5}O_3$ (LZT) with the high dielectric constant, high loss and positive τ_f ceramics $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ were investigated to achieve zero τ_f values and the structure evolution were also studied.[7–14] Near zero τ_f was obtained in these compositions at the cost of Q.f degradation along with improvement in dielectric constant values. The structure also transformed from monoclinic $P2_1/n$ to orthorhombic Pbnm with B-site disorder. Structural changes including cation ordering was suggested as determining factor for the sign of τ_f in LZT based perovskite systems.[13] Tamura[14] concluded that dielectric loss tangent at microwave frequency is mainly caused by the anharmonic terms in the crystal's potential energy, and increased by lattice defects such as disordered charge distribution.

In this paper, $La(Mg_{0.5}Sn_{0.5})O_3$ (LMS) ceramics are synthesized by solid-state reaction method to achieve high quality factors. X-ray diffraction data is obtained using X'celerator detector with Real time multiple strip (RTMS) technology. Structure of LMS is also investigated using Rietveld analysis. The initial model for the refinement is obtained from Structure Prediction and Diagnostics Software[15] (SPuDS). Microwave dielectric measurements are also carried out on LMS samples.

2. Experimental procedure

$La(Mg_{0.5}Sn_{0.5})O_3$ powders were prepared by mixed oxides method from individual high-purity oxides La_2O_3 (Alfa Aesar, 99.99%), MgO (Cerac, 99.95%) and SnO_2 (Cerac, 99.9%). The starting materials were weighed according to stoichiometry after drying La_2O_3 at 1000 °C for 24 h and MgO at 800 °C for 3 h to remove moisture content and carbonates. The powders were dry mixed with an agate mortar and pestle and then subsequently wet mixed using distilled water medium. The wet mixed powder is dried in an oven at 150 °C for 6 h. Calcination was carried out at

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1200 °C for 6 h with an intermediate mixing. Calcined powder with the organic binder was pressed into pellets using uniaxial press and binder was evaporated at 500 °C for 12 h. Sintering was carried out at 1500, 1550 and 1600 °C for 4 h.

X-ray diffraction data was collected using PaNAlytical X'pert pro MPD in Bragg-Brentano geometry with X'celerator detector. The collection conditions were Cu Kα-radiation, 40 kV 30 mA, 0.017° step scan, 1.0° divergence slit and 0.02 rad. incident and receiving soller slits. Data was collected in 2θ ranges of 15–105° with the total collection time of 50 min. Densities of the samples were measured using Archimedes method.

Microwave dielectric measurements were performed using HP8720A Network Analyzer. TE_{011} or $TE_{01\delta}$ mode was used for the measurements. The dielectric constant (ε_r) was measured using the Hakki–Coleman[16] dielectric resonator method as modified and improved by Courtney.[17] Quality factor (Q.f) was measured using reflection mode gold coated copper cavity. Temperature coefficients of dielectric resonators were measured using a temperature controlled hot plate enclosure with an invar cavity in the temperature range of 30–70 °C.

3. Results and discussion

3.1. X-ray diffraction pattern and super lattice reflections

The Goldschmidt tolerance factor of LMS is 0.93 and the bond valence tolerance factor obtained from SPuDS[15] is 0.91, indicates that ion size of La^{3+} is too small to occupy the space between octahedrons. The low tolerance factor with small size of La^{3+} is responsible for octahedral tilting.

Fig. 1 shows the X-ray diffraction pattern of the LMS ceramics sintered at 1600 °C and the inset shows splitting in 1 1 0 peak. All the peaks were indexed based on a cubic perovskite cell. A series of extra peaks were observed corresponding to super lattice reflections. According to Glazer[18] the super lattice reflections, with specific combinations of odd (o) and even (e) Miller indices point to definite types of deviation of the structure from

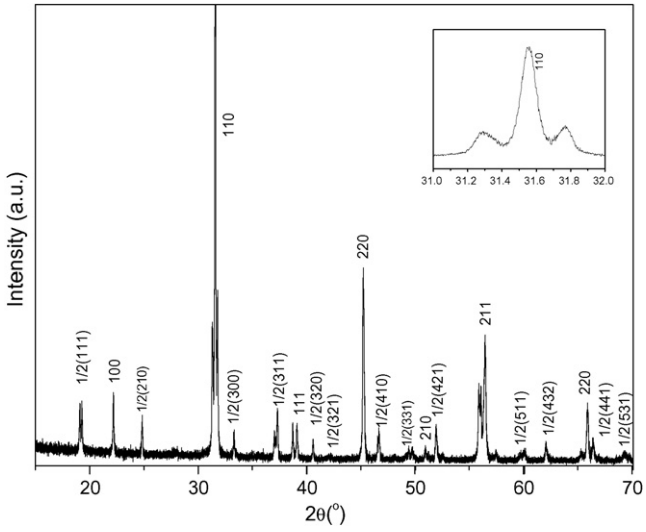

Fig. 1. X-ray diffraction pattern of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics.

the undistorted cubic one such as octahedral in-phase tilting (ooe, eoe, eeo), anti-phase tilting (ooo, $h+k+l>3$), chemical ordering (ooo) and anti-parallel displacement of A-cations (eoe, eeo, oee).

The extra reflection $\frac{1}{2}(1\,1\,1)$ in X-ray pattern is due to the ordering of B-site cations. The ordering peak is clearly observed in LMS compared to LMT[2] as scattering length difference between Mg^{2+} and Sn^{4+} is higher than that of Mg^{2+} and Ti^{4+}. The reflections corresponding to out of phase tilting ($\frac{1}{2}(3\,1\,1)$, $\frac{1}{2}(3\,2\,1)$, $\frac{1}{2}(3\,3\,1)$ and $\frac{1}{2}(5\,3\,1)$), in phase tilting ($\frac{1}{2}(3\,2\,1)$) and A-site cation displacement ($\frac{1}{2}(2\,1\,0)$, $\frac{1}{2}(3\,2\,0)$, $\frac{1}{2}(4\,1\,0)$, $\frac{1}{2}(2\,1\,0)$ and $\frac{1}{2}(4\,3\,2)$) were also observed. Splitting was also observed in reflection peaks 1 1 0, 1 1 1 and 2 2 0, which are indicating lowering of the symmetry. The presence of in-phase tilting, out of phase tilting and splitting in reflections suggest that LMS is a B-site ordered monoclinic $P2_1/n$ with $a^-a^-c^+$ tilting system.

3.2. Structure determination

The Rietveld refinement was carried out using GSAS[19] suite with EXPGUI[20] interface and the starting model for the refinement was obtained from SPuDS.[15] The refinement assuming complete ordering resulted $R_{wp}=7.44$, $R_p=5.67$ and $\chi^2=1.161$ with negative thermal parameter of Mg and high thermal parameter of Sn, which clearly indicates that the ordering is not complete. Similar kind of behavior was previously observed in the case of $La(MgTi)_{0.5}O_3$.[7] By allowing the Mg/Sn disorder in the refinement using the constraints, refinement was improved with $R_{wp}=7.33$, $R_p=5.55$ and $\chi^2=1.128$. The fractional occupancy of most occupied B-site ion is determined to be 0.94. The degree of cation ordering is quantified with the long-range order parameter (LRO)

$$\mathrm{LRO} = [2 \times (\mathrm{occ.})_B - 1] \times 100 \quad (1)$$

where $(occ.)_B$ is the fractional occupancy of B-site cation on the predominantly occupied octahedral site.[21] The LRO is determined to be 89% with $(occ.)_B=0.9445$ where as it is 92% with reported $(occ.)_B=0.96$ for both LMT[7] and $Nd(MgTi)_{0.5}O_3$ (NMT).[22] The LRO of LMS is expected to be less than that of LMT as the ionic size difference between Mg^{2+} and Sn^{4+} (0.03 Å) is less than that of the size difference between Mg^{2+} and Ti^{4+} (0.11 Å).

The final Rietveld refinement plot obtained is shown in Fig. 2 and the refined structure is shown in Fig. 3. Lattice parameter and fractional atomic coordinates resulted from the refinement were presented in Table 1 and selected interatomic distances compared to those calculated using ionic radii by Shannon[23] are presented in Table 2. The theoretical density obtained is 6.631 g/cm^3. Bond valences are calculated using the program Valence.[24] The bond valences of La^{3+} is 2.74, Mg^{2+} is 2.12 and Sn^{4+} is 3.95.

3.3. Microwave dielectric properties

The relative density and microwave dielectric properties of LMS were investigated as a function of sintering temperature

Table 1
Refined lattice parameters, fractional atomic coordinates and thermal parameters of $La(MgSn)_{0.5}O_3$ ceramics

Lattice parameters: $a = 5.6385(3)$ Å, $b = 5.7228(3)$ Å, $c = 8.0209(4)$ Å and $\beta = 90.0737(5)^\circ$; fractional atomic coordinates, thermal parameters and occupancy					
Atoms	x	y	z	Occupancy	100 U (Å^2)
La	0.4888(5)	0.5409(1)	0.2501(2)	1	0.919(1)
Mg(1)	0.0000	0.500	0.000	0.9445(4)	0.593(4)
Sn(1)	0.500	0.000	0.000	0.9445(4)	0.529(1)
Mg(2)	0.500	0.000	0.000	0.0555(4)	0.593(4)
Sn(2)	0.000	0.500	0.000	0.0555(4)	0.529(1)
O(1)	0.280(2)	0.280(2)	−0.058(3)	1	0.288(3)
O(2)	0.217(2)	0.801(2)	−0.040(4)	1	0.288(3)
O(3)	0.593(2)	−0.024(1)	0.256(2)	1	0.288(3)

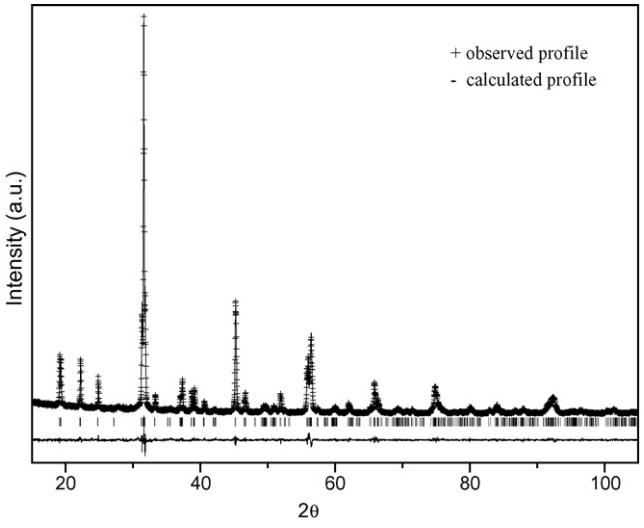

Fig. 2. Observed and refined X-ray diffraction pattern.

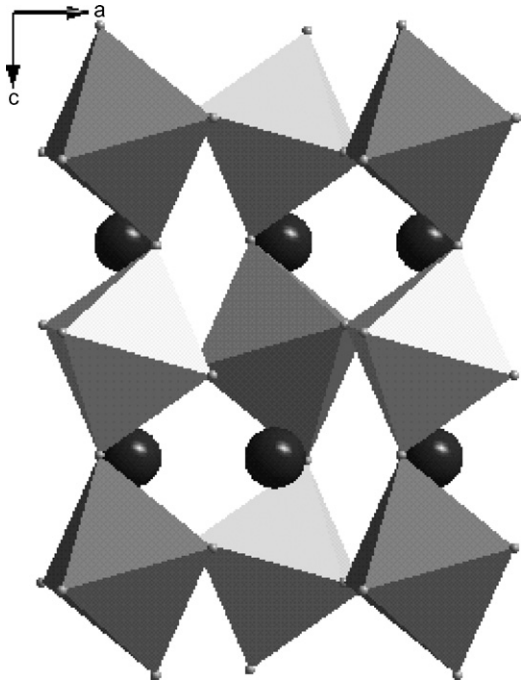

Fig. 3. Crystal structure of $La(MgSn)_{0.5}O_3$ viewed along the *b* direction. Magnesium octahedra are in light-gray, Tin octahedra are in dark-gray and black shaded circle is Lanthanum.

Table 2
Selected atomic distances (Å) of $La(MgSn)_{0.5}O_3$ ceramics

MgO_6-octahedron	
Mg/Sn-O(1) × 2	2.075
Mg/Sn-O(2) × 2	2.141
Mg/Sn-O(3) × 2	2.027
Mean	2.081
Shannon	2.12
SnO_6-octahedron	
Sn/Mg-O(1) × 2	2.081
Sn/Mg-O(1) × 2	1.985
Sn/Mg-O(1) × 2	2.129
Mean	2.065
Shannon	2.09
LaO_8-polyhedron	
La-O(1) × 1	2.438
La-O(1) × 1	2.558
La-O(1) × 1	2.980
La-O(2) × 1	2.718
La-O(2) × 1	2.458
La-O(2) × 1	2.809
La-O(3) × 1	2.558
La-O(3) × 1	2.385
Mean	2.61
Shannon	2.76

(Table 3). The relative density increased with sintering temperature. The density of the ceramic sintered at 1600 °C is maximum with 98.6% of the theoretical density. The dielectric constant is around 20. Both the dielectric constant and Q.f values increased with increase in sintering temperature, which is due to increase in density with sintering temperature. The dielectric constant of LMT sintered at 1600 °C is 28 with Q.f product 61,000.[2] Dielectric constant of LMS is less than that of LMS, which is attributed to the low polarizability of the Sn compared to Ti. By the contribution of anharmonic terms in the crystal's potential energy, the lower ε_r material exhibits higher Q.f value.[14] Hence, in general, decrease of dielectric constant increases Q.f value. But signifi-

Table 3
Microwave dielectric properties of $La(MgSn)_{0.5}O_3$ ceramics

Temperature (°C)	Rel. density (%)	ε_r	Q.f (GHz)	τ_f (ppm/°C)
1500	97.7	19.5	44,200	−74
1550	98.2	19.7	56,300	−80
1600	98.6	20.1	63,000	−78

cant improvement of quality factor in LMS is not observed over LMT, which may be due to low percentage of LRO in LMS compared to LMT. Further investigations on phonon modes are required to know the exact reason.

The temperature coefficient of resonant frequency does not show any systematic variation and is largely negative which is expected as LMS is having both in phase tilting and out of phase tilting.[25] The correlation of dielectric properties with bond valences is under investigation.

4. Conclusions

$La(MgSn)_{0.5}O_3$ samples with high density are synthesized using solid-state reaction method. Rietveld refinement of XRD data obtained with X'celerator detector is carried out and analysis revealed that $La(MgSn)_{0.5}O_3$ has a monoclinic structure ($P2_1/n$ space group) corresponding to $a^-a^-c^+$ tilting with $a = 5.6385$ Å, $b = 5.7228$ Å, $c = 8.0209$ Å and $\beta = 90.0737^\circ$. The B-site disorder is also refined and long-range order is determined to be 89%. Bond valences of La^{3+}, Mg^{2+} and Sn^{4+} are calculated to be 2.74, 2.19 and 3.95, respectively.

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