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$La(Mg_{1/2}Ti_{1/2})O_3$–$La_{2/3}TiO_3$ microwave dielectric ceramics

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Abstract

Structure and microwave dielectric properties were studied in the $(1-x)La(Mg_{1/2}Ti_{1/2})O_3$–$xLa_{2/3}TiO_3$ system. Ceramics with this composition in the $0 \leqslant x \leqslant 0.5$ range were processed from powders obtained by a citrate-based chemical route. Structure of these perovskite solid solutions changed from orthorhombic for $x=0.1$ and 0.3 to pseudocubic for $x=0.5$. Microwave and radio frequency measurements revealed increase in permittivity and temperature coefficient of the resonant frequency τ_f with increasing of $La_{2/3}TiO_3$ content. Close to zero τ_f value was found near to $x=0.5$ composition of $(1-x)La(Mg_{1/2}Ti_{1/2})O_3$–$x\ La_{2/3}TiO_3$.

Keywords: Dielectric properties; Perovskites; Resonator; Sintering

1. Introduction

A considerable group of materials for microwave applications is based on solid solutions with the perovskite structure. Wide possibilities of atomic substitutions and/or formation of cation and anion vacancies mean it is possible to obtain complex perovskite system with desired properties. Important dielectric characteristics in the microwave range, like permittivity (ε_r), quality factor (Q) and thermal coefficient of the resonant frequency (τ_f) can be adjusted by choosing the appropriate end members and varying the composition. On the other hand, the τ_f, ε_r and Q dependences in solid solutions are often non-linear and even non-monotonic.[1–3] Correlations between structure and microwave dielectric characteristics of perovskite compounds (e.g. τ_f) have been revealed only for some particular compositions[4,5] and are not common. Therefore, the compositional behaviour of the earlier parameters in many solid solutions is difficult to predict.

La_2O_3–TiO_2-based perovskite ceramics have been found to be of great interest as prospective materials for production of the microwave resonators.[6–9] In this family $La(Mg_{0.5}Ti_{0.5})O_3$ (LMT) is characterized by a monoclinic perovskite structure due to oxygen octahedra tilting, La displacement, as well as Mg/Ti ordering.[6–8] The LMT ceramics were found to give $\varepsilon_r=27.4$, Q = 10 500 at 7 GHz and $\tau_f \sim -80$ ppm/°C.[8,10] The orthorhombic structure of $La_{2/3}TiO_3$ (LT) is considered as "double perovskite" because its parameters are $a \sim a_0$, $b \sim a_0$ and $c \sim 2a_0$.[11] The c-axis length is doubled due to the ordered arrangement of the La^{3+} cations and vacancies in the A-site of the perovskite lattice. Owing to the high vacancy content, the perovskite phase of pure LT is unstable and therefore its dielectric properties have been studied in the solid solutions with other oxide compounds.[11,12] For the composition $x=0.96$ of the $(1-x)CaTiO_3-xLT$ solid solutions, the dielectric resonator characteristics were $\varepsilon_r=90$, Q = 2700 (at 10 GHz) and $\tau_f=190$ ppm/°C.[11] These parameters were found to change monotonically with x. In the $(1-x)LaAlO_3$–xLT system, in which orthorhombic $LaAlO_3$ has a negative thermal coefficient of the resonant frequency, the monotonic dependence of both permittivity and τ_f were also observed.[12] High ε_r and Q values together with τ_f close to zero were obtained at microwave frequencies in compositions near $x=0.6$.

This work aims to study the structure and microwave dielectric properties of perovskite ceramics with $(1-x)La(Mg_{0.5}Ti_{0.5})O_3$–$xLa_{2/3}TiO_3$ composition. This system is of a direct practical interest because the end members have τ_f with opposite signs. Regarding microwave properties, $La(Mg_{0.5}Ti_{0.5})O_3$ is close to $LaAlO_3$ and therefore one can expect a similar behaviour of the dielectric parameters in the solid solutions with LT, namely monotonic dependence of ε_r and τ_f on composition as well as $\tau_f \sim 0$ for a suitable composition.

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2. Experimental

$(1-x)$LMT–xLT ($x=0$, 0.1, 0.3 and 0.5) solid solutions were processed from powders obtained by a citrate-based chemical route.[10] Calcined powders were uniaxially pressed into disks of 10 mm in diameter and about 1 mm in thickness and sintered either in air or an oxygen gas flow, at temperatures ranging from 1450 to 1550 °C for 2 h. The heating and cooling rates were 10 °C/min in every case. For microwave dielectric measurements, cylindrical samples of 10 mm in diameter and 8–10 mm length were isostatically pressed and sintered under the same conditions.

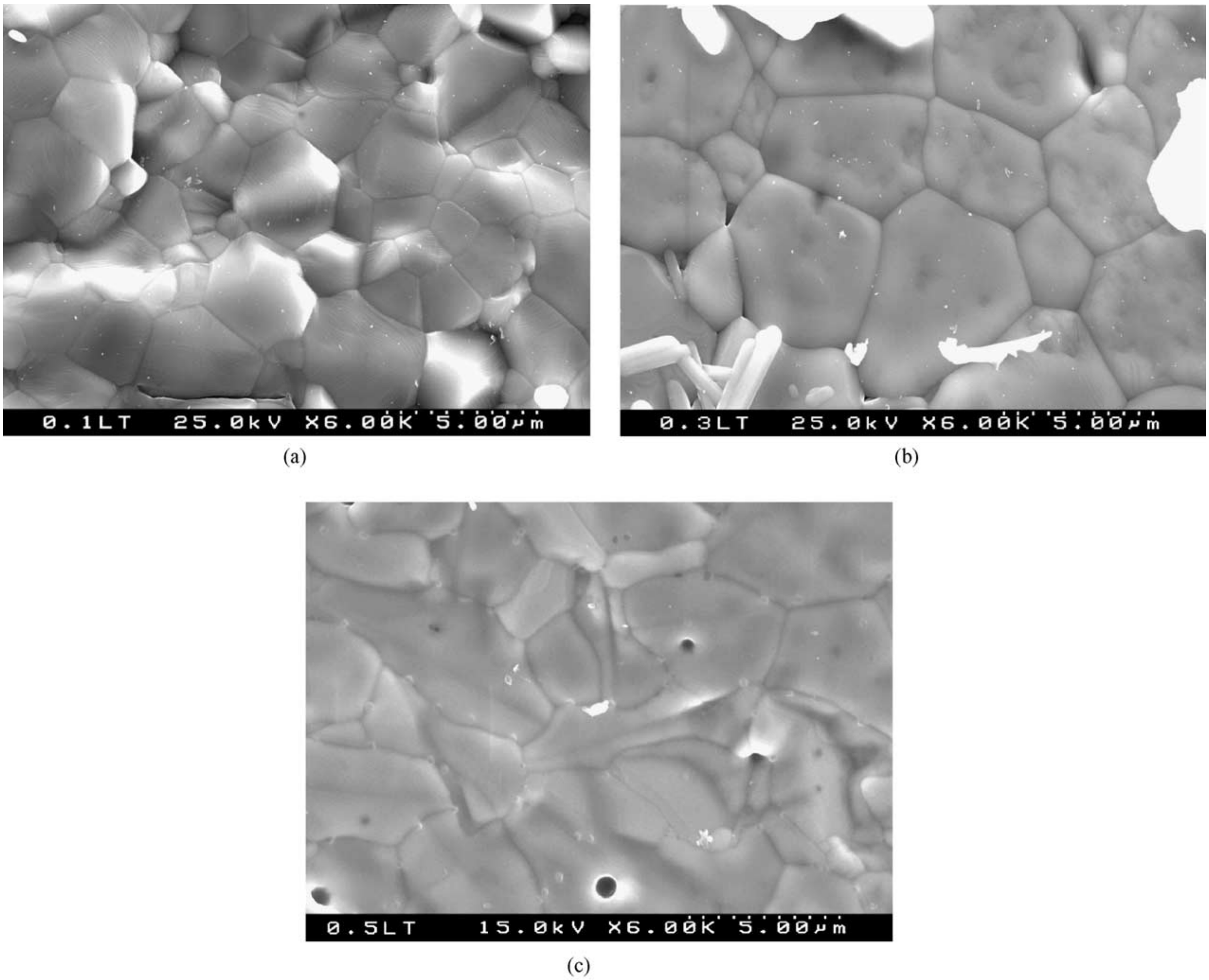
The phase identifications and the determination of the crystal lattice parameters of the solid solutions were carried out by X-ray diffraction (XRD) with Cu $K\alpha$ radiation (Rigaku D/MAX-B diffractometer). Ceramic microstructures were studied by scanning electron microscopy (SEM, Hitachi S-4100).

To measure low frequency dielectric properties, polished pellets of 0.5–0.7 mm in thickness were electroded with platinum paste followed by annealing at 800 °C. Dielectric permittivity and loss tangent were measured as a function of temperature at a frequency range of 10^2–10^6 Hz, using Precision LCR meter (HP 4884A). Measurements were performed over the interval 25–300 °C using a heating rate of 1.5 °C/min. Microwave dielectric properties of the samples were estimated at room temperature by an adaptation of the Hakki–Coleman method[13,14] using 10 MHz–20 GHz scalar analyser (IFR 6823).

3. Results and discussion

Microstructures of the $(1-x)$LMT–xLT ceramics for $x=0.1$, 0.3, 0.5 are shown in Fig. 1. As can be seen, dense ceramics were obtained with the earlier-mentioned sintering conditions. Densities of the samples were measured to be between 95 and 97% in terms of relative density.

Fig. 2 shows powder XRD patterns of the $(1-x)$LMT–xLT ceramics. The Rietveld analysis, revealed that solid solutions presented the perovskite



(a) (b) (c)

Fig. 1. SEM photographs of the $(1-x)$LMT–xLT ceramics sintered: (a) $x=0.1$, (b) $x=0.3$ (2 h at 1500 °C) and (c) $x=0.5$ (2 h at 1400 °C).

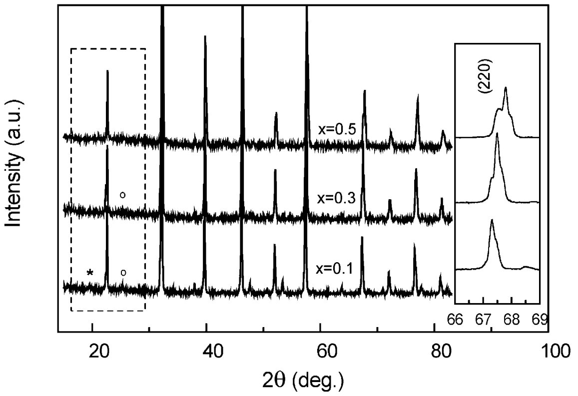


Fig. 2. XRD patterns of the (1−x)LMT–xLT ceramics at room temperature. Superlattice reflections indicating Mg/Ti ordering (stars) and antiparallel La displacement (circles) are shown.

orthorhombic structure for $x=0.1$ and 0.3. An increase of vacancies in the perovskite A-sites in accordance with the chemical composition $La_{(1-x/3)x/3}Mg_{(1-x)/2}Ti_{(1+x)/2}O_3$ was confirmed by the good fit between observed and calculated patterns. A gradual elimination of the superlattice reflections (Fig. 2) testifies the decrease of both Mg/Ti ordering degree and antiparallel La displacements as the LT content is increased.

Reflection lines in the XRD pattern of the samples with composition $x=0.5$ were too complex to be indexed individually (see inset of Fig. 2). The lines were therefore indexed as a cubic perovskite to evaluate average cell parameter.

Cell parameter evolution in the $0\leqslant x\leqslant 0.3$ range is shown in Fig. 3. Note that with small increase of LT content, parameter **a** becomes larger than **b** as has been already observed in solid solutions between LMT and other titanates ($BaTiO_3$[15] and $SrTiO_3$[16]). Such dependence of the parameters is found to happen regardless of whether the unit cell volume increases or decreases with composition. Moreover, our preliminary XRD studies as a function of temperature revealed the same behaviour of **a**(T) and **b**(T). This phenomenon deserves further study.

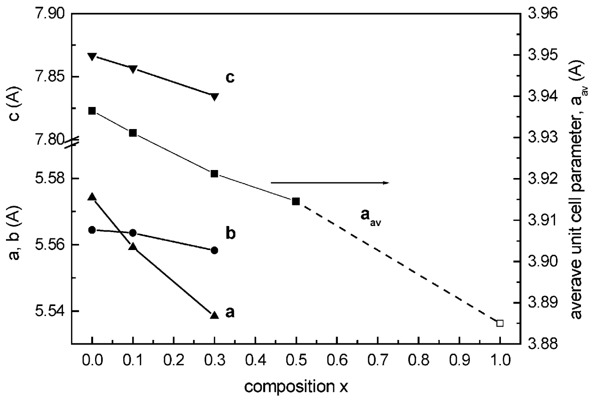


Fig. 3. Variation of the (1−x)LMT–xLT cell parameters with composition. The open symbol corresponds to value taken from.[17]

The average unit cell parameter (a_{av}), reduced to one formula unit, decreases almost linearly in the range $0\leqslant x\leqslant 0.5$ (Fig. 3). For comparison, the a_{av} value corresponding to $x=1$ is also plotted. It should be noted that cell parameters of the LT have been found to be strongly affected by oxygen content.[17] Depending on sintering conditions because of partial reduction of Ti^{4+}, the cell parameters of the LT (i.e. $La_{2/3}TiO_{3-\delta}$) changed considerably. The observed increase of cell volume with δ is related to electrostatic repulsion of unscreened cations in the crystal lattice due to the O^{2-} anion loss.[17]

Low-frequency dielectric permittivity as a function of temperature showed no anomalies or frequency dispersion in the range 10^2–10^6 Hz. Plots of $\varepsilon_r(T)$ were almost linear, so the thermal coefficient of capacitance (τ_c) and ε_r value at room temperature were evaluated. To estimate τ_f of the ceramic under investigation, the relation $\tau_f=-[\alpha_L+\tau_c]/2$ was used. Here the linear thermal-expansion coefficient (α_L) is known to be between 9 and 12 ppm/°C for perovskites.[18] A value of 10 ppm/°C was taken for the τ_f estimation.

Dielectric permittivity, the $Q\times f_0$ value and thermal coefficient of the resonant frequency are plotted in Fig. 4.

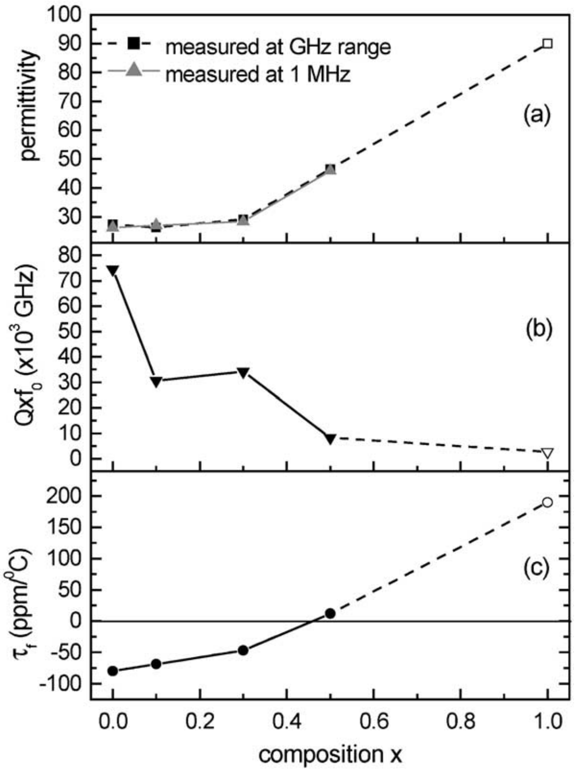


Fig. 4. (a) Relative permittivity, (b) $Q\times f_0$ values, (c) τ_f, as a function of×for solid solutions (1−x)LMT–xLT. Open symbols are denoted data from.[11]

It is evident that ε_r measured at microwave frequency and at 1 MHz show the same behaviour with increasing LT content. Differences between ε_r values for each composition was found to be less than 4%. As can see from Fig. 4, τ_f, ε_r and Qxf_0 change almost monotonically and these trends are in good agreement with corresponding data for LT.[11]

It has been found that microwave losses in the LT-based ceramics could be reduced by oxygen annealing[11] or by oxygen sintering.[19] Indeed, annealing air-sintered ceramics of 0.5LMT–0.5LT composition in the O_2 flow led to an increase of Q by almost a factor of two without a permittivity change. However, for ceramics with smaller LT content this improvement in Q value was almost negligible. The relatively higher loss in these ceramics (comparing with that in the $LaAlO_3$–LT system)[12,19] appears to be connected with higher Ti content. The low Q value seems to arise from reduction of the Ti^{4+} cation during the high temperature sintering in air. Similar phenomena have occurred in high ε_r/low Q microwave ceramics of the $CaTiO_3$–LT system.[11]

4. Conclusion

Solid solutions in the system $(1-x)$LMT–xLT were obtained in the $0 \leqslant x \leqslant 0.5$ range. The ceramics were processed from powders obtained by a citrate-based chemical route. Densities of samples were found to be 95–97% of theoretical. XRD spectra showed that the solid solutions exhibit orthorhombic structure for $x = 0.1$ and 0.3 and pseudocubic for $x = 0.5$.

The dielectric properties, characterized at microwave (GHz) and radio (MHz) frequencies, showed an increase in relative permittivity with increasing LT content. The coefficient τ_f showed a monotonic behaviour with composition, becoming zero near the composition with $x = 0.5$.

The comparatively low Q value of air-sintered ceramics seems to be connected with reduction of Ti^{4+} during sintering at elevated temperatures. The Q value of the 0.5LMT–0.5LT composition could be improved by oxygen annealing. For ceramics with smaller LT content the effect of oxygen annealing was negligible.

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