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Microwave dielectric properties of Bi-substituted $La(Mg_{1/2}Ti_{1/2})O_3$

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Abstract

The system $La(Mg_{1/2}Ti_{1/2})O_3$–$Bi(Mg_{1/2}Ti_{1/2})O_3$ (LMT–BMT) was investigated in respect to formation of perovskite solid solutions based on lanthanum magnesium titanate. Single-phase perovskite $(1-x)$LMT–xBMT ceramics ($0 \le x \le 0.3$) were prepared and their crystal structure and dielectric properties were studied. It has been found that within the solubility range the crystal structure of Bi-substituted LMT remains monoclinic, $P2_1/n$. Unit cell volume was evaluated to be almost independent on x, varying within the experimental error. Relative permittivity of the ceramics increases by almost a factor of 3 in the range $0 \le x \le 0.3$ and its value is 40–45 at the compositional region where temperature coefficient of the resonant frequency passes a zero-value. Compositional and temperature variations of the dielectric parameters for LMT–BMT estimated at different frequency ranges are considered in comparison with those observed in other Bi-substituted ceramics based on LMT.

Keywords: $La(Mg,Ti)O_3$; Sintering; X-ray methods; Dielectric properties; Perovskites

1. Introduction

One can postulate two main advantages of bismuth(III) oxide to be involved in dielectric ceramics. First, a high polarizability of Bi^{3+} cation (similar to that of Pb^{2+}) allows developing ferroelectrically active materials, which possess the properties comparable with those of the best lead-containing compositions. Concerning dielectric ceramics for microwave application, doping with bismuth is expected to increase their relative permittivity (ε_r) and compensate temperature coefficient of the resonant frequency (τ_f) at a gigahertz range. Second, owing to the low melting point of Bi_2O_3, it can serve as an aid to decrease the sintering temperature.

Low-loss ordered perovskite $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) is a promising microwave dielectric composition. At the same time, its ε_r and τ_f (27 and −81 ppm/C, respectively[1]) could be improved. Mixing with an appropriate end member is known to be one of the ways to tune the microwave dielectric characteristics in such materials. High-ε_r and near zero-τ_f compositions have been found in the LMT-based solid solutions with ferroelectrics[1,2] and incipient ferroelectrics.[3,4] Furthermore, based on these systems as model objects, an effect of A-, B-site substitutions and cation vacancies on the crystal structure and the resulting microwave dielectric properties was investigated. Similarly, Bi-substituted LMT ceramics are also expected to be attractive in these respects.

There is no substantial difference between La^{3+} and Bi^{3+} cations in terms of both size and charge. However, unlike LMT, $Bi(Mg_{1/2}Ti_{1/2})O_3$ (BMT) cannot be synthesized as a single phase at normal pressure.[5] It is known that Bi^{3+} possesses a $6s^2$ lone-pair electronic configuration and has a propensity for a covalent chemical bond. This feature seems to be a reason why many of the bismuth-based compositions adopt a perovskite structure in special conditions only, e.g. under high pressure. Nevertheless, "$Bi(Mg_{1/2}Ti_{1/2})O_3$" has successfully been used as a virtual perovskite end member in air-sintered solid solutions based on $PbTiO_3$ with morphotropic phase boundary.[6,7] Hence, one can expect at least a partial solubility BMT in LMT at normal pressure.

This work reports on preparation, structure refinement, and dielectric characterization of the perovskite ceramics in the $(1-x)$LMT–xBMT system ($0 \le x \le 0.3$).

2. Experimental

The conventional mixed oxides method was used to prepare the $(1-x)$LMT–xBMT ceramics with the nominal compositions $0 \le x \le 0.5$. A stoichiometric mixture of the respective reagent-grade oxides and carbonates was ball-milled in ethanol

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and calcined at 750 °C (for 4 h) and then at 950 °C (4 h) with intermediate re-grindings. The powders were then isostatically pressed to obtain disks of 10 mm in diameter and about 1 mm thick (for radio-frequency measurements) as well as cylinders of 8–12 mm length (for microwave measurements). The samples were then sintered in air at the temperatures ranged from 1200 to 1550 °C, depending on composition. Dwell time was 4 h; heating and cooling rates did not exceed 5 °C/min in every case. Relative density of the obtained ceramics was determined by Archimedes method and their microstructure was examined by scanning electron microscopy (SEM). The samples for the SEM examinations were polished and thermally etched 50 °C below their sintering temperature for 2 min.

Phase analysis of the ceramics and crystal structure determination were performed by X-ray diffraction (XRD) from the powders of the samples ground. XRD data were collected at room temperature using a Rigaku D/MAX-B diffractometer (Cu Kα radiation, tube power 40 kV, 30 mA, graphite monochromator). The Rietveld refinement of the obtained data was performed using the FULLPROF suite.[8]

The samples for dielectric investigations at radio frequency range were polished to form disks with a thickness of 0.4–0.5 mm, electroded with platinum paste and annealed at 1000 °C. Dielectric permittivity and loss tangent were measured as a function of temperature within the range of 10^2 to 10^6 Hz using a Precision LCR meter (HP 4284A). The measurements were performed over the interval −178 to 210 °C on both heating and cooling with a rate of 1.5 °C/min in an environment chamber (Delta Design 9023). The room-temperature permittivity, quality factor (Q) and resonant frequency (f_0) of the samples at a microwave frequency range were estimated by an adaptation of the Hakki–Coleman method[9,10] using a 10 MHz to 20 GHz Scalar Analyzer (IFR 6823).

3. Results and discussion

It was inferred from the XRD data of the sintered $(1-x)$LMT–xBMT samples that a single perovskite phase exists up to $x = 0.3$. At higher Bi content the second phases, namely $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$, were detected along with the main perovskite phase (Fig. 1). A limited solubility observed in the system is not unexpected considering the above-mentioned instability of the perovskite BMT at normal pressure.[5]

A comparison of the XRD patterns of the $(1-x)$LMT–xBMT samples ($0 < x < 0.3$) revealed that these patterns are qualitatively identical to that of LMT. It has been proved[11] that the crystal structure of the lanthanum magnesium titanate perovskite is characterized by the monoclinic $P2_1/n$ space group. Whole set of the superstructure reflections associated with the structure distortions in LMT was also observed in the XRD patterns of the obtained ceramics (Fig. 1). These reflections indicate the presence of the rocksalt-type of B-cation ordering, A-cation antiparallel displacements as well as both in-phase and anti-phase oxygen octahedral tilting. Moreover, no regular variation in intensity of the superstructure reflections was detected when increasing x from 0 to 0.3. One may conclude that the crystal

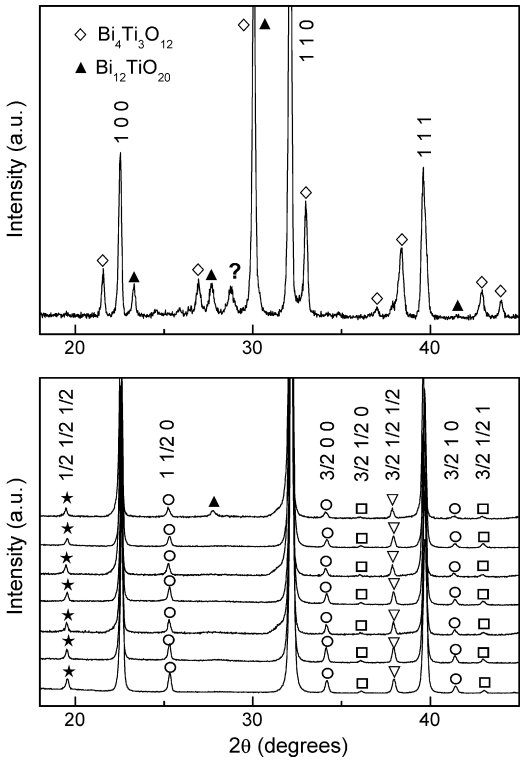

Fig. 1. Top panel: XRD pattern of $(1-x)$LMT–xBMT with $x = 0.5$. Bottom panel: XRD patterns of the compositions $x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 (from bottom to top) with the superstructure reflections indicating Mg/Ti ordering (⋆), antiparallel A-cation displacements (◯), in-phase octahedral tilting (□), and anti-phase octahedral tilting (▽). The indexing is presented in the primitive perovskite unit cell.

structure of perovskite LMT is not changed when substituting bismuth for lanthanum up to the solubility limit. Indeed, the crystal structure of the ceramics was successively refined using the $P2_1/n$ space group with the correct description of all the XRD profiles. Unit cell volume (V) of the $(1-x)$LMT–xBMT perovskites was found to be almost independent on x. The value of V showed no systematic change, varying within the experimental error. Based on the refined structure data and the unit cell relations reported in Ref. 4, the parameters of the primitive perovskite unit cell were also calculated. As a result of the above-mentioned structure distortions in LMT–BMT, the primitive perovskite unit cell of these solid solutions is characterized by the pseudo-triclinic metric (with the parameters $a_p = c_p \neq b_p$ and $\alpha_p = \gamma_p \neq \beta_p$). These are presented in Fig. 2 as a function of Bi content. The structure data for pure LMT ($x = 0$) were taken from Ref. 11 where a non-conventional chemical route was used for preparation of this composition. It should be noted that the difference in values of the structure parameters for LMT reported by Avdeev et al. 11 and Lee et al. 12 was estimated to be about 0.4%. For comparison, the maximal relative variation of the most variable parameter, b_p, for Bi-substituted LMT is less than 0.45%.

Density of the sintered ceramics was measured to be between 92 and 94% in terms of the theoretical density. SEM observations also testified to dense and single-phase ceramics in the LMT–BMT system (Fig. 3).

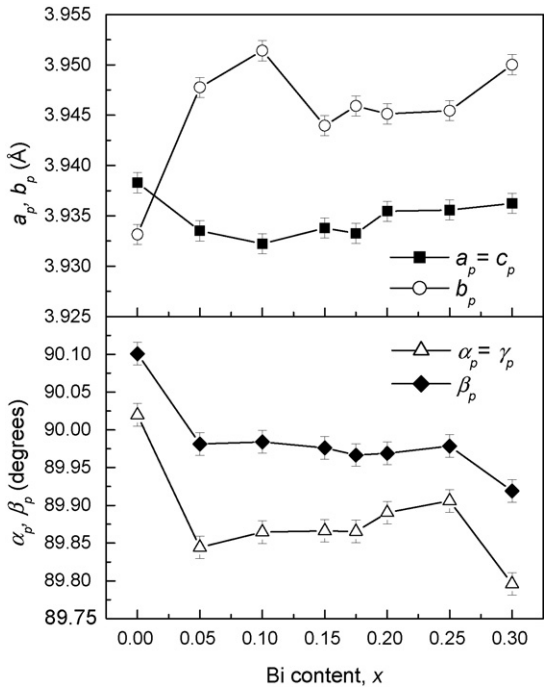

Fig. 2. Parameters of the primitive perovskite unit cell (a_p, b_p, c_p and α_p, β_p, γ_p) as a function of Bi content in the $(1-x)$LMT–xBMT system.

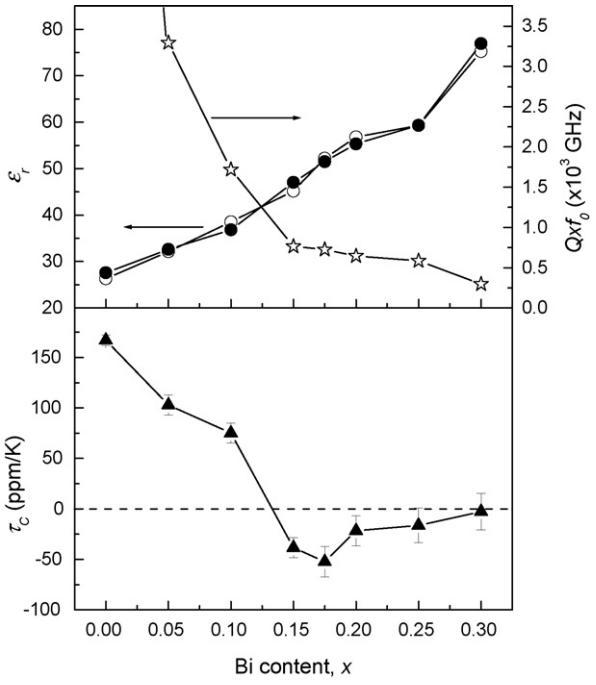

Fig. 4. Dielectric characteristics of the $(1-x)$LMT–xBMT ceramics as a function of x: ε_r (circles); Qf_0 (stars); τ_C (triangles), measured at a gigahertz range (open symbols) and at 10^6 Hz (solid symbols).

Relative permittivity of the $(1-x)$LMT–xBMT ceramics measured at a gigahertz range is presented in Fig. 4 as functions of x. It is seen that compositional variation of ε_r is close to a hyperbolic-type and its magnitude increases by almost a factor of three in the range $0 \le x \le 0.3$. Room-temperature values of the relative permittivity were also estimated from the temperature dependences at radio frequencies (Fig. 5). The values of ε_r estimated at different frequency ranges are evidently in good agreement (see Fig. 4). Hence, one can suppose that their temperature variations are also essentially similar. At the ranges, where $\varepsilon_r(T)$ for all the compositions varies almost linearly (between about 25 and 180 °C, Fig. 5), the thermal coefficient of capacitance (τ_C) was evaluated. The values of τ_f were

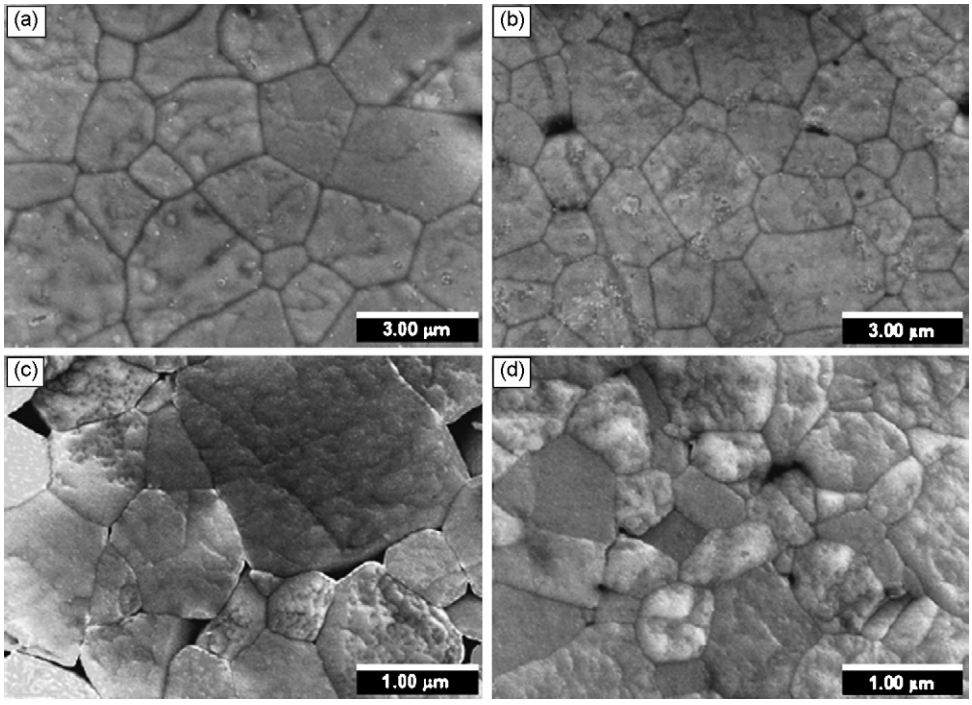

Fig. 3. SEM images of polished and thermally etched surfaces of the $(1-x)$LMT–xBMT ceramics: $x = 0.05$ (a); 0.15 (b); 0.25 (c); 0.30 (d).

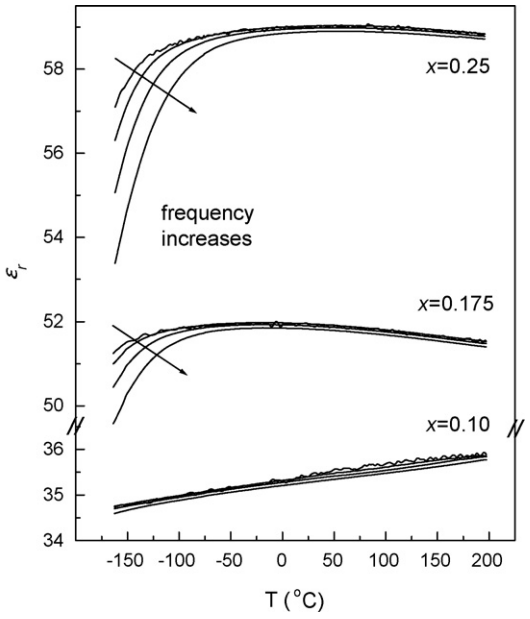

Fig. 5. Temperature dependences of relative permittivity of the $(1-x)$LMT–xBMT ceramics in the range of 10^3 to 10^6 Hz.

then determined by using the relation $\tau_f = -1/2[\tau_C + \alpha_L]$.[13] The linear thermal-expansion coefficient (α_L) was assumed to be 10 ppm/C, as its value is ordinarily in the range of 9–12 ppm/C for most perovskites.[14] Indeed, the values of τ_f evaluated in such way were found to be very close to those directly measured at microwave range.[1,3]

Compositional dependence of τ_C for the $(1-x)$LMT–xBMT system is also shown in Fig. 4. Estimation using the measured τ_C values and the above relation yielded a zero-τ_f value for the $(1-x)$LMT–xBMT ceramics with x between 0.10 and 0.15. Taking into account the observed nearly monotonic behaviours of both ε_r and τ_C when x is increased to 0.175, one may conclude that the variation of the temperature coefficient of capacitance in this compositional range is mainly governed by dilution of the average ionic polarizability.[15] Further increase of Bi content results in a change in the character of the $\tau_C(x)$ dependence (Fig. 4). It is known that the structure transformations involving oxygen octahedral tilting affect a slope of $\varepsilon_r(T)$ of a particular composition and thereby control both magnitude and sigh of its τ_C.[14,15] However, no phase transition was detected in the $(1-x)$LMT–xBMT system generally and in the vicinity of $x = 0.175$ specifically. As seen from Fig. 5, low temperature parts of the $\varepsilon_r(T)$ curves are frequency-dependent. The temperature range, where the permittivity (both real and imaginary parts) of the $(1-x)$LMT–xBMT ceramics is frequency-dispersive, regularly shifts with x, that is certainly associated with the amount of Bi in the system. In spite of the observed compositional increase of the relative permittivity at $x \geq 0.175$, the negative slope of the $\varepsilon_r(T)$ curves becomes less in magnitude. In fact the curves are the most rounded (convex) for the compositions in the immediate vicinity of $x = 0.175$. Similar behaviour of the dielectric response was recently observed in the LMT–$(Na_{1/2}Bi_{1/2})TiO_3$ (NBT) ceramics.[2] In this system, the range of the frequency-dependent behaviour is also shifted when increasing NBT content. The range was observed to transform into the dispersive shoulder on the $\varepsilon_r(T)$ curve followed by the diffuse maximum typical of NBT-rich compositions.[16] Contribution of the localized charge hopping conduction induced by an increasing amount of Bi in the LMT-BMT ceramics could be one more reason for the change in the slope of the $\varepsilon_r(T)$ curves. Whatever the case, this phenomenon certainly needs a particular investigation.

Compositional variation of the quality factor expressed in terms of Qf_0 is presented in Fig. 4 as a function of Bi content. It is known that the microwave loss in dielectric materials is influenced in many respects by the processing conditions. For instance, the Qf_0 values for LMT prepared using the conventional ceramic method[12] and by the chemical route[3] were reported to be 63,100 and 114,000 GHz, respectively. However, even if considering the lowest value, the quality factor of the LMT ceramics decreases by a factor of 20 at as low as 5% substitution with bismuth. As also seen from Fig. 4, Qf_0 keeps on lowering with further increase of x. It should be noted that the quality factor for the LMT–BMT ceramics follows a similar trend and its value is of the same order of magnitude (for the equal rates of Bi-substitutions) as that of LMT–NBT.[2] It seems, therefore, that nature and behaviour of the microwave dielectric loss in both systems should be considered in the same context and using supplementary methods, such as dielectric and far-infrared spectroscopies. An optimization of the preparation procedure of these Bi-substituted dielectric ceramics could be also attempted.

4. Conclusions

Limited solubility ($0 \leq x \leq 0.3$) was observed in the perovskite $(1-x)$LMT–xBMT system. When $x > 0.3$, the second phases, $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$, appear in addition to the perovskite phase. Crystal structure of the Bi-substituted LMT ceramics is characterized by the monoclinic symmetry with $P2_1/n$ space group allowing for cation ordering and oxygen octahedral tilting over the whole range of existence. The observed compositional behaviour of the crystal lattice parameters suggests that the structure of $(1-x)$LMT–xBMT is mainly governed by the La-based matrix.

The values of relative permittivity measured at megahertz and gigahertz frequency ranges are in good agreement. The observed variation of ε_r with Bi content is close to a hyperbolic-type. In spite of unchanging crystal structure of the LMT–BMT solid solutions, their values of temperature coefficient of capacitance at radio frequencies demonstrate a non-monotonic dependence. The low-temperature dielectric response of the $(1-x)$LMT–xBMT ceramics is frequency-dependent. The appearance and localization of the dispersive ranges are certainly governed by amount of Bi in the system. This dielectric relaxation process as well as conduction of the localized charge carriers seem to be the most probable reasons for the $\tau_C(x)$ behaviour observed in $(1-x)$LMT–xBMT.

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