Journal of Alloys and Compounds 500 (2010) 190–194

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

New material properties of xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$ ($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics at microwave frequencies

Yuan-Bin Chen*

Department of Engineering & Management of Advanced Technology, Chang Jung Christian University, 396 Chang Jung Rd., Sec. 1, Kway Jen, Tainan 71101, Taiwan

ARTICLE INFO

Article history:
Received 17 February 2010
Received in revised form 22 March 2010
Accepted 30 March 2010
Available online 8 April 2010

Keywords:
Dielectric
Dielectric resonators
Microwave ceramics

ABSTRACT

Ceramics in the system xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 with B_2O_3 additions (1 wt.%) have been investigated by the conventional solid-state route. Doping with B_2O_3 (1 wt.%) can effectively promote the densification and the dielectric properties of xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$ ($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics. 0.4La($Mg_{1/2}Ti_{1/2}$)O_3–0.6($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics with 1 wt.% B_2O_3 addition possesses a dielectric constant (ε_r) of 42, a Qxf value of 33,000 GHz (at 8 GHz) and a temperature coefficient of resonant frequency (τ_f) of 0.5 ppm/°C sintering at 1475 °C. As the content of La($Mg_{1/2}Ti_{1/2}$)O_3 increases, the highest Qxf value of 56,000 (GHz) for x = 0.8 is achieved at the sintering temperature 1500 °C.

1. Introduction

Recently, the La-modified complex perovskites attracted a great attention as promising microwave dielectrics. One of the important characteristics of such materials is the temperature coefficient of resonant frequency (TCF), which should be as close to zero as possible for the successful application in thermally stable electronic devices. It was previously shown that La($B'_{1/2}B''_{1/2}$)O_3 perovskites presenting oxygen octahedral tilt and B′/B″ ordering have negative TCF while alkaline-earth-metal titanates have a positive one. Therefore, the preparation of solid solutions between those compositions is a promising way to obtain materials with TCF close to zero [1].

A class of perovskite-related non-ferroelectric materials is known to be appropriate for microwave applications. Owing to their ability to form solid solutions in a wide range of substituting atoms, perovskites are intensively explored as basic compositions to obtain materials with controlled properties. A series of low-loss perovskite system have been investigated and adjusted for microwave applications. However, the most widespread method for producing new materials is still an empirical one and slow progress is observed in discovering and clarifying mechanisms controlling microwave dielectric parameters in complex systems. Correlations between structure and microwave dielectric characteristics of perovskite compounds have only been revealed for some particular compositions [2].

Among many candidates, the complex A(B′B″)O_3 perovskite materials have been extensively studied due to their excellent dielectric properties and unique order–disorder behavior. In A(B′B″)O_3 complex perovskite materials, there are 1:2 and 1:1 ordering according to the arrangement of B site cations. The arrangement of 1:2 and 1:1 ordering means two kinds of B site cations repeated as B′B″B″B′B″B″ and B′B″B′B″, respectively. In general, 1:1 ordering and 1:2 ordering of B sites occur in A($B'_{1/2}B''_{1/2}$)O_3- and A($B'_{1/3}B''_{2/3}$)O_3-based materials, respectively [3]. 1:2 ordering has been found mainly in Ba($B'_{1/3}B''_{2/3}$)O_3-based perovskite materials (e.g., Ba($Zn_{1/3}Ta_{2/3}$)O_3) and is known to strongly influence microwave dielectric properties. It has been reported that substitutions with cation dopants may change the 1:2 ordering into the local 1:1 ordering depending on perovskite composition and annealing condition. In contrast to 1:2 ordering, 1:1 ordering is expected to occur in A($B'_{1/2}B''_{1/2}$)O_3 type perovskites [3]. 1:1 ordering at B site has been reported earlier in several low frequency dielectric materials including Pb($Mg_{1/3}Nb_{2/3}$)O_3.

In this study, with a positive ($Na_{0.5}Nd_{0.5}$)TiO_3 τ_f value was introduced to into the mixture form a solid solution xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 to compensate for the τ_f value.

It is expected that the combination of two different perovskites of ($Na_{0.5}Nd_{0.5}$)TiO_3 (ε_r of around 98, Qxf value higher than 7000 GHz and a τ_f value of +260 ppm/°C) [4] and La($Mg_{0.5}Ti_{0.5}$)O_3 (ε_r of 27, a Qxf value of 114,000 GHz, and a negative τ_f of −81 ppm/°C) [5] generates the complex perovskite structure which results from the occurrence of co-substitution at A and B sites as the content of La($Mg_{0.5}Ti_{0.5}$)O_3 increases relative to that of ($Na_{0.5}Nd_{0.5}$)TiO_3. In this study, xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 system

* Fax: +886 6 335981.
E-mail address: cubnck@yahoo.com.tw.

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doi:10.1016/j.jallcom.2010.03.239

based on $(Na_{0.5}Nd_{0.5})TiO_3$ and $La(Mg_{0.5}Ti_{0.5})O_3$, both having the perovskite structure, has been investigated microwave dielectric properties.

However, pure $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics require a very high sintering temperature (1600 °C). There are three approaches to reduce the sintering temperature of microwave dielectric ceramics: low melting sintering aids addition [6–8], chemical processing, and the use of smaller particles as the starting materials. In this paper, B_2O_3 was used as a sintering aid for reducing the sintering temperature of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics. The effects of B_2O_3 on the sintering and microwave dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics were investigated.

2. Experimental procedure

The $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ powders were prepared by the solid-state reaction method by mixing individual high-purity oxide La_2O_3, Nd_2O_3, MgO, B_2O_3, Na_2O and TiO_2. The starting materials were stoichiometrically weighed after drying La_2O_3 and Nd_2O_3 at 1000 °C for 24 h and MgO at 800 °C for 6 h to remove moisture content and carbonates. The powders were then dry mixed with an agate mortar and pestle and subsequently wet mixed using distilled water. Each wet mixed powder was dried in an oven at 130 °C for 6 h. The calcination temperature was varied between 1100 and 1200 °C for 4 h. The calcined powder with the organic binder polyvinyl alcohol was pressed into pellets using a uniaxial press and the binder was evaporated at 650 °C for 12 h. Sintering was carried out at 1400–1500 °C for 4 h. The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochrometer in the 2θ range of 20–60°. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL–40FEG).

The bulk densities of the sintered pellets were measured by the Archimedes method. Microwave dielectric properties such as dielectric constant and unloaded Q were measured at 6–12 GHz by the post-resonant method as suggested by Hakki and Coleman [9]. This method consisted of parallel conducting plates and coaxial probes on the TE_{011} mode. TE means transverse electric waves and the first two subscript integers denote the wave guide mode, while the third integer denotes the order of resonance in an increasing set of discrete resonant lengths. The temperature coefficient of resonant frequency was measured in the temperature range of 20–80 °C. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of 1 wt.% B_2O_3-doped $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics at various sintering temperatures (1400–1500 °C). In Fig. 1, no secondary phases can be observed since detection of a minor phase by X-ray is extremely difficult. The existence of some superlattice peaks with low intensities needed to be confirmed using high-resolution XRD patterns. The evidence of anti-phase tilting was found for all compositions particularly from the (3 1 1) reflections [10]. The (3 3 1) reflections also corresponding to the anti-phase tilting began to appear of 1 wt.% B_2O_3-doped $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ (Fig. 1). XRD patterns of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramic systems form solid solution, and all peaks match with $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ compound.

The SEM photographs of $0.4La(Mg_{1/2}Ti_{1/2})O_3–0.6(Na_{0.5}Nd_{0.5})TiO_3$ ceramics sintered at various temperatures for 4 h are illustrated in Fig. 2. For all compositions, low level porosity and densed ceramic could be observed in the figure. The degree of the grain growth increased with the increase of sintering temperature. Porous specimens could not be observed for all sintered ceramics. It may play an important role to degrade the lattice vibration and get the high Q value. However, $0.4La(Mg_{1/2}Ti_{1/2})O_3–0.6(Na_{0.5}Nd_{0.5})TiO_3$ inhomogeneous grain growth was observed at temperatures higher than 1500 °C with 1 wt.% B_2O_3 additive, which might degrade the microwave dielectric properties of the ceramics. At 1500 °C, the phenomenon of abnormal grain growth occurs in soap foams and

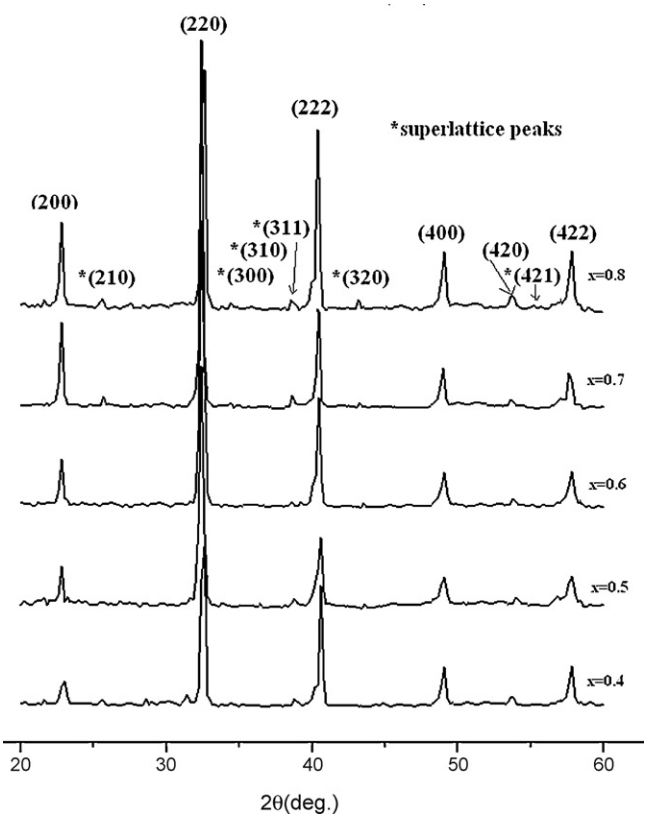


Fig. 1. X-ray diffraction patterns of $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics with 1 wt.% B_2O_3 addition sintered at 1500 °C.

polycrystalline ceramics for example. The driving force in these systems is the surface tension which leads to a reduction of the total surface area of the grains. Grain growth is the process that takes place during annealing of polycrystalline materials; its major feature is a systematic increase in grain size. Two different types of grain growth can be distinguished: the normal and abnormal grain growth. On the contrary, when the abnormal grain growth is the dominant mechanism, there are certain grains (abnormal grains) in the microstructure that grow much faster than the majority of the grains and in the end consume the fine-grained matrix around them. There has been a lot of work done in the field of abnormal grain growth, but the actual mechanism of abnormal grain formation and development from a uniform grain size distribution is not fully understood.

Fig. 3 shows typical energy dispersive X-ray (EDX) for $0.4La(Mg_{1/2}Ti_{1/2})O_3–0.6(Na_{0.5}Nd_{0.5})TiO_3$ ceramics at 1450 °C. The surfaces of samples were coated by Pt. EDX analysis was used in combination with scanning electron microscopy to distinguish each different grain. The grain morphology of $0.4La(Mg_{1/2}Ti_{1/2})O_3–0.6(Na_{0.5}Nd_{0.5})TiO_3$ ceramics exhibited solid solution without any second phase.

The density of the B_2O_3-doped $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics sintered at various temperatures as shown in Fig. 4. It indicated that densities of 4.1–5.74 (g/cm^3) were obtained for B_2O_3-doped $xLa(Mg_{1/2}Ti_{1/2})O_3–(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics at sintering temperatures from 1400 to 1500 °C. The sintering temperatures were determined on the basis of the apparent densities of the solid solutions. The densities of specimen for $x = 0.4$ and $x = 0.8$ are shown in Fig. 4. All specimens have high relative densities over 95% sintering above 1475 °C. Bulk densities are increased with increase of x because of the higher density of $La(Mg_{1/2}Ti_{1/2})O_3$.

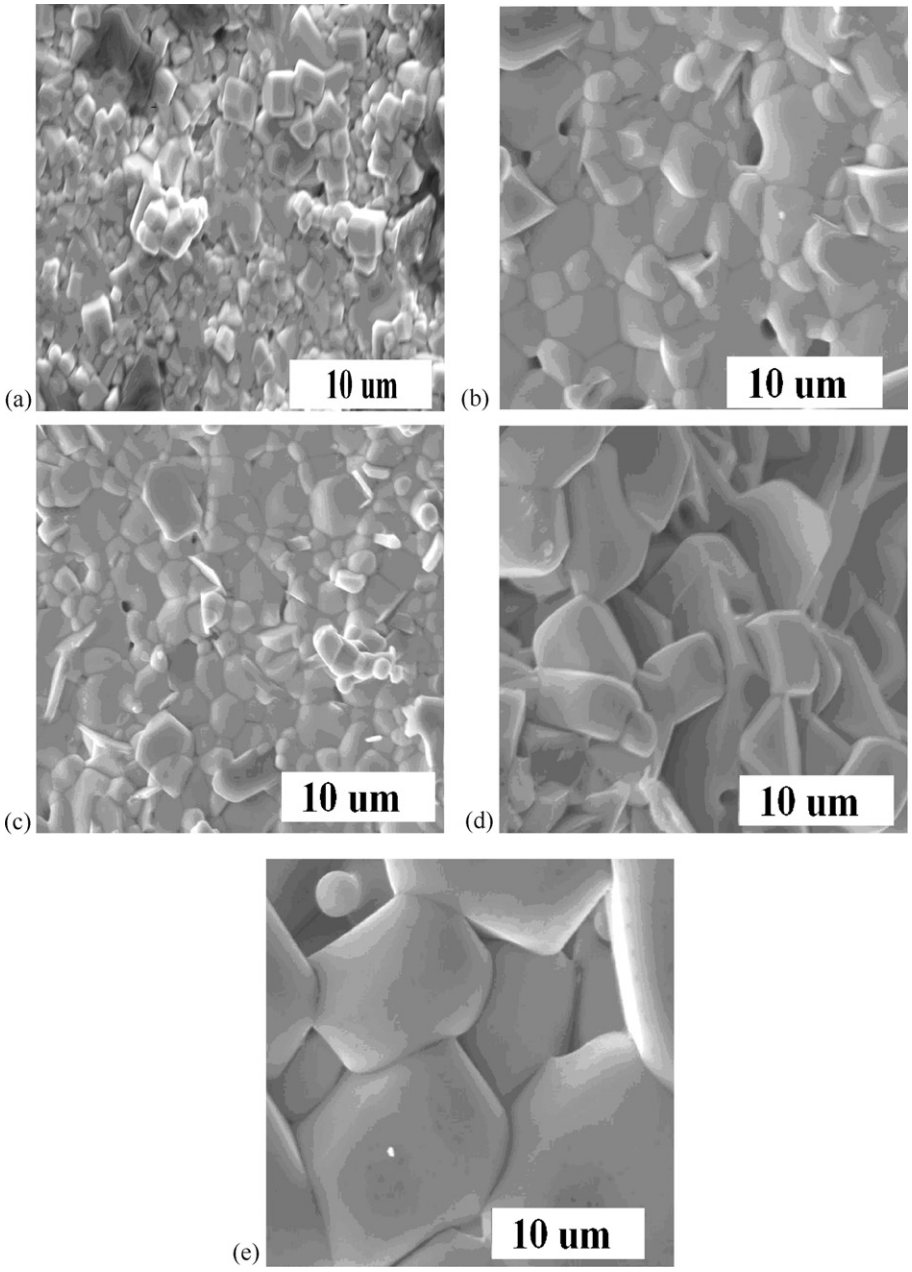


Fig. 2. SEM photographs of $0.4La(Mg_{1/2}Ti_{1/2})O_3$–$0.6(Na_{0.5}Nd_{0.5})TiO_3$ ceramics sintered at (a) 1400 °C, (b) 1425 °C, (c) 1450 °C, (d) 1475 °C and (e) 1500 °C with 1 wt.% B_2O_3 additions for 4 h.

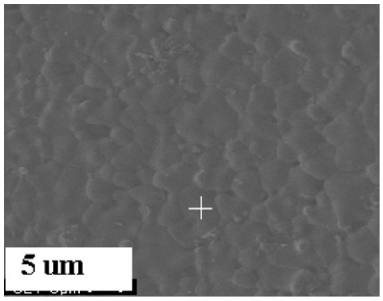
The dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ with 1 wt.% B_2O_3 addition are illustrated in Fig. 5. As the x value increased from 0.4 to 0.8, the dielectric constants decreased from 42 to 28. The dielectric constants slightly decreased with increasing sintering temperature above 1475 °C due to over-sintering of $0.4La(Mg_{1/2}Ti_{1/2})O_3$–$0.6(Na_{0.5}Nd_{0.5})TiO_3$. With 1 wt.% B_2O_3 addition, a ε_r value of 42 was obtained for $0.4La(Mg_{1/2}Ti_{1/2})O_3$–$0.6(Na_{0.5}Nd_{0.5})TiO_3$ ceramics sintered at 1450 °C.

Fig. 6 displays the *Qxf* values of $(Na_{0.5}Nd_{0.5})TiO_3$ ceramics with 1 wt.% B_2O_3 additions at different sintering temperatures as functions of the x values which had a maximum value at 1500 °C. The *Qxf* value increases with the increase of $La(Mg_{1/2}Ti_{1/2})O_3$ content and sintering temperature. It was expected since that the quality factor of $La(Mg_{1/2}Ti_{1/2})O_3$ is much higher than that of $(Na_{0.5}Nd_{0.5})TiO_3$ and the bulk density increased with increasing sintering temperature due to the ceramics being denser. Many factors could affect the microwave dielectric loss of dielectric resonators such as the lattice vibration modes, the pores and the secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and the dielectric loss was thus reduced. It seems that the dielectric loss of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics system was dominated by the bulk density and the grain size. The highest *Qxf* value of 56,500 (GHz) for $x = 0.8$ is achieved at the sintering temperature 1500 °C.

The temperature coefficients of the resonant frequency (τ_f) of B_2O_3-doped $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)(Na_{0.5}Nd_{0.5})TiO_3$ ceramics at different sintering temperatures are illustrated in Fig. 7. The temperature coefficient of resonant frequency is well known related to the composition, the additives and the second phase of the material. It seemed that higher $(Na_{0.5}Nd_{0.5})TiO_3$ content would shift the τ_f value to more positive. It varied from −52 to 0.5 ppm/°C as the amount of $(Na_{0.5}Nd_{0.5})TiO_3$ addition increased from 0.4 to 0.8

Table 1
Structural data for sintered xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($La_{0.5}Nd_{0.5}$)TiO_3.

	Anti-phase tilting	In-phase tilting	Tolerance factor	(1 1 1)Mg/Ti ordering	Space group
$x=0.4$	o	x	0.9560	x	*Pbnm*
$x=0.5$	o	x	0.9543	x	*Pbnm*
$x=0.6$	o	o	0.9527	x	*Pbnm*
$x=0.7$	o	o	0.9511	x	*Pbnm*
$x=0.8$	o	o	0.9494	o	*Pbnm*



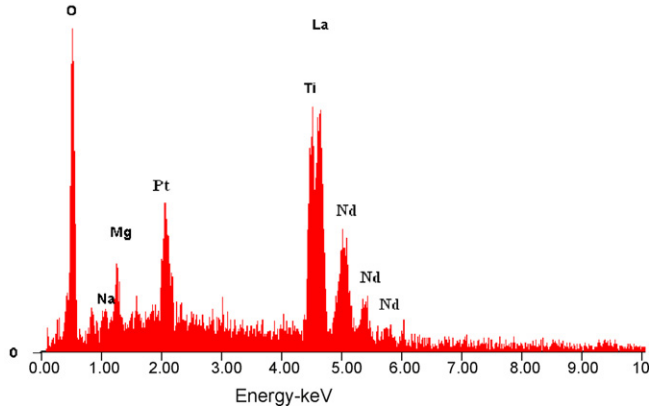


Fig. 3. EDX data of 0.4La($Mg_{1/2}Ti_{1/2}$)O_3–0.6($Na_{0.5}Nd_{0.5}$)TiO_3 sintered at 1475 °C.(atom%): Na K: 9.24, La L: 17.64 Nd L: 10.08, Ti K: 26.8, O K: 24.8, Mg K: 8.1

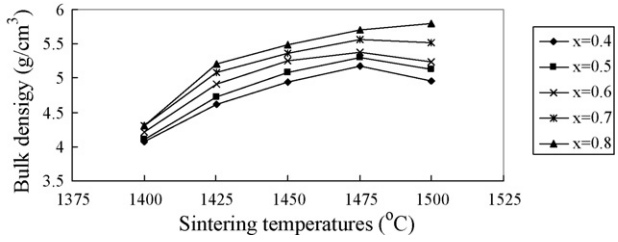


Fig. 4. Bulk density of xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics system sintered at different temperatures with 1 wt.% B_2O_3 addition.

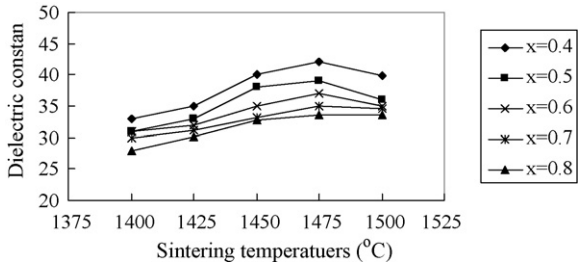


Fig. 5. ε_r values of xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics system sintered at different temperatures with 1 wt.% B_2O_3 addition.

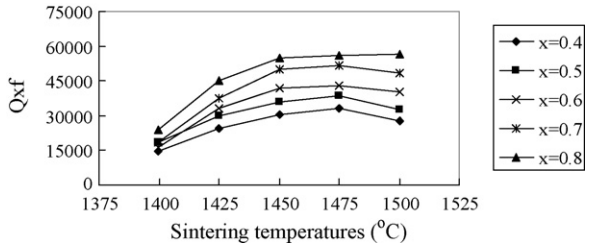


Fig. 6. *Qxf* values of xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics system sintered at different temperatures with various 1 wt.% B_2O_3 addition.

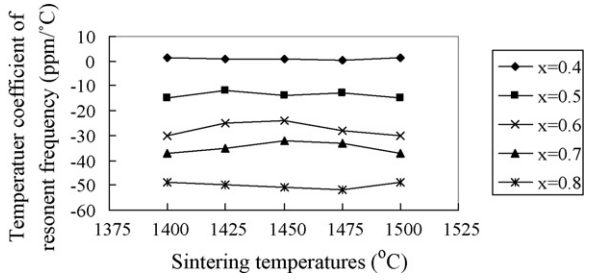


Fig. 7. Temperature coefficient values of xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics system sintered at different temperatures with 1 wt.% B_2O_3 addition.

sintered at 1475 °C. In general, the temperature coefficient of the resonant frequency was found to be related to the composition and the existing phase in ceramics.

Table 1 includes the tolerance factor of each composition and the (1 1 1) superlattice reflection due to the 1:1 ordering. The tolerance factor t, which is given by $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$ in the ABO_3 perovskite, was calculated after taking the average ionic sizes of each site for both ($Na_{0.5}Nd_{0.5}$)TiO_3 and La($Mg_{1/2}Ti_{1/2}$)O_3. The tolerance factor decreased with increasing La($Mg_{1/2}Ti_{1/2}$)O_3, which can be expected from the main contribution of the relatively large size of Mg^{2+} ion at the B site. The tolerance factor is known to be correlated with structural symmetry and tilting of the octahedral in perovskites [10,11]. The decrease of t with increasing La($Mg_{1/2}Ti_{1/2}$)O_3 is correlated to the decrease of TCF as shown in Fig. 7. In the tilted region, generally the increasing thermal energy is completely absorbed to recover the tilting. This is reasonable when considered the difference in TCF values of pure ($Na_{0.5}Nd_{0.5}$)TiO_3 and La($Mg_{1/2}Ti_{1/2}$)O_3 (+260 and −65 ppm/°C, respectively). TCF is also known to follow the mixing rule in most cases as the dielectric constant does.

4. Conclusions

The dielectric properties of B_2O_3-doped xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics were investigated. xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)$($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics exhibited perovskite structure. With 1 wt.% B_2O_3 addition, a dielectric constant of 42, a *Qxf* value of 33,000 (GHz) and a τ_f value of 0.5 ppm/°C were obtained for 0.4La($Mg_{1/2}Ti_{1/2}$)O_3–0.6($Na_{0.5}Nd_{0.5}$)TiO_3 ceramics at 1475 °C for 4 h. The decrease

in *Qxf* value at higher sintering temperature was owing to that the grain boundary phases were pronounced product. Therefore, the B_2O_3-doped $0.4La(Mg_{1/2}Ti_{1/2})O_3$–$0.6(Na_{0.5}Nd_{0.5})TiO_3$ ceramic is suitable for applications in microwave dielectric resonators and microwave devices because of its excellent microwave dielectric properties.

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