Journal of Alloys and Compounds 509 (2011) 6285–6288

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Structure and dielectric characterization of xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ in the microwave frequency range

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ARTICLE INFO

Article history:
Received 18 February 2011
Received in revised form 7 March 2011
Accepted 9 March 2011
Available online 16 March 2011

Keywords:
Ceramics
Sintering
Grain size

ABSTRACT

The crystal structures, phase compositions and the microwave dielectric properties of the xLa($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.8}Sr_{0.2}TiO_3$ composites prepared by the conventional solid state route have been investigated. The formation of solid solution is confirmed by the XRD patterns. Doping with B_2O_3 (0.5 wt.%) can effectively promote the densification and the dielectric properties of xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics. It is found that xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics can be sintered at 1375 °C, due to the liquid phase effect of B_2O_3 addition observed by Scanning Electronic Microscopy. At 1375 °C, 0.4Nd($Mg_{1/2}Ti_{1/2}$)O_3–0.6$Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with 1 wt.% B_2O_3 addition possesses a dielectric constant (ε_r) of 49, a $Q\times f$ value of 13,000 (at 8 GHz) and a temperature coefficients of resonant frequency (τ_f) of 1 ppm/°C. As the content of Nd($Mg_{1/2}Ti_{1/2}$)O_3 increases, the highest $Q\times f$ value of 20,000 GHz for x = 0.9 is achieved at the sintering temperature 1400 °C.

1. Introduction

The dielectric properties of perovskite compounds are strongly related to their structural characteristics, such as cation ordering and the orientation of the oxygen octahedra [1]. Recently, complex perovskites and their solid solutions were investigated and found to be promising dielectrics for microwave applications [2]. Dielectric materials for microwave applications should, in general, satisfy three conditions: high permittivity, low dielectric loss, and small temperature coefficient of resonant frequency (τ_f). These properties can be understood in terms of the structural characteristics. The permittivity of dielectrics can be calculated using the Clausius–Mossotti relation and additivity rule; however, structural factors, such as cation compression or rattling, can induce a difference between the calculated and measured permittivity [3]. Cation ordering has a great effect on the dielectric loss and phase transition characteristics of complex perovskites.

Although most dielectric ceramics with high dielectric constants have positive τ_f values, material with a high dielectric constant, high Q and negative τ_f are desired to achieve this goal. Jong-Hee Kim et al. have reported many complex perovskites $A(B_{1/2}^{2+}B_{1/2}^{4+})O_3$ with negative τ_f [4]. Among them, Nd($Mg_{1/2}Ti_{1/2}$)O_3 has a high dielectric constant ($\varepsilon\sim27$), a high quality factor ($Q\times f$ value ~ 46,000 GHz) and a negative τ_f value (−49 ppm/°C). $Ca_{0.6}La_{0.8/3}TiO_3$ (ε_r = 100, $Q\times f$ = 20,000 GHz, τ_f = 212 ppm/°C) [5–8] with a positive τ_f value was introduced to into the mixture form a solid solution xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ to compensate for the τ_f value.

In previous studies, La($Mg_{1/2}Ti_{1/2}$)O_3 sintering temperature as high as 1650 °C. In this work, B_2O_3 was selected as a sintering aid to lower the sintering temperature of xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics. The crystalline phases, the microstructures and the microwave dielectric properties of B_2O_3-doped xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics were investigated. Mixtures of xNd($Mg_{1/2}Ti_{1/2}$)O_3 and $Ca_{0.6}La_{0.8/3}TiO_3$ ceramics were employed to obtain a new dielectric material system with a high dielectric constant, a high $Q\times f$ value and a near-zero temperature coefficient of resonant frequency. The dielectric properties and microstructures of the xNd($Mg_{1/2}Ti_{1/2}$)O_3 and $Ca_{0.6}La_{0.8/3}TiO_3$ ceramic system were also evaluated.

2. Experimental

Samples of xNd($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ were synthesized by conventional solid state method. The starting materials were mixed according to a stoichiometric ratio. A small amount of B_2O_3 (1 wt.%) was added as a sintering aid. High purity oxide powders (>99.9%) Nd_2O_3, Nd_2O_3, MgO, $CaCO_3$, TiO_2 and B_2O_3 were weighed and mixed for 24 h with distilled water. The mixture was dried at 100 °C and thoroughly milled before it was calcined at 1200 °C for 4 h. The calcined powder was ground and sieved through 100-mesh screen. Phase formation of xNda($Mg_{1/2}Ti_{1/2}$)O_3–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ was confirmed using X-ray diffraction. The calcined powders were then re-milled for 24 h with PVA solution as a binder. Pellets with 11 mm in diameter and 5 mm in thickness were pressed using uniaxial pressing. A pressing pressure of 2000 kg/cm^2 was used for all samples. After debinding, these pellets were sintered at temperatures 1300–1400 °C for 3 h in air. The

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doi:10.1016/j.jallcom.2011.03.056

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. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki and Coleman [9] dielectric resonator method as modified and improved by Courtney [10]. The dielectric resonator was positioned between two brass plates. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25 °C to +80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf),

$$\tau_f = \frac{f2 - f1}{f1(T2 - T1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

X-ray diffraction patterns recorded from $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ $(0.4 \le x \le 0.9)$ compositions sintered at their optimum sintering temperatures for 4 h are shown in Fig. 1. All the peaks were indexed based on the perovskite unit cell. All the peaks were indexed based on the perovskite unit cell. Second phase was not observed at the level of 1 wt.% B_2O_3 addition since that detection of a minor phase by X-ray is extremely difficult. Fig. 1 shows XRD patterns of $\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramic systems form solid solution, and all peaks match with $\mathrm{Nd}(\mathrm{Mg}_1\mathrm{Ti}_{1/2})\mathrm{O}_3$–$\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ compound. The lattice parameters and unit-cell volumes of $\mathrm{Nd}(\mathrm{Mg}_1\mathrm{Ti}_{1/2})\mathrm{O}_3$–$\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics are presented in Table 1. Employing the calculated lattice parameters (Table 1). No reflections of impurity phases were observed and therefore the formation of solid solutions in all the range can be concluded. The shift in 2θ values observed in this figure is due to the smaller lattice parameters of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$.

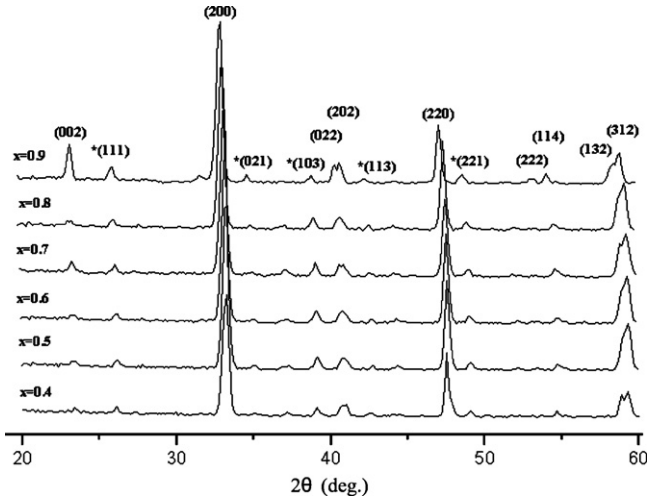

Fig. 1. X-ray diffraction patterns of $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics with 1 wt.% B_2O_3 addition sintered at 1435 °C for 3 h.

Table 1
Cell parameters of $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ with 1 wt.% B_2O_3 addition ceramics sintered at 1375 °C for 3 h.

x value	a (Å)	b (Å)	c (Å)	Unit cell volume (Å^3)	Space group
0.3	5.417	5.443	7.672	226.20	Pbnm
0.5	5.429	5.456	7.689	227.75	Pbnm
0.7	5.457	5.507	7.736	232.47	Pbnm
0.9	5.461	5.562	7.769	235.97	Pbnm

The compositions with $x = 0.4$–0.9 also present an orthorhombic structure. The variation of the cell parameters with respect to the amount of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ shows a linear decreased with the increase of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ content. The parameters were found to be in very good agreement with those reported [11–14] for three other compositions of $\mathrm{Nd}(\mathrm{Mg}_1\mathrm{Ti}_{1/2})\mathrm{O}_3$–$\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ system. The cell volume gradually decreases with x according to the substitution of Nd^{3+} and Mg^{2+} by the smaller Ca^{2+}, La^{3+} and Ti^{4+} respectively.

The spectra for all the compositions were indexed according to an orthorhombic unit cell with space group Pbnm (no. 62, cab nonstandard setting for Pnma). Combinations of odd (O) and even (E) reflections indicate a distorted perovskite structure (individual peaks are identified by numbers in brackets). On the basis of Glazer's notation, the (OOE, OEO, and EOO) reflections are assigned to an in-phase tilting of the oxygen octahedra surrounding the B-site cations. The (OOO) reflections are assigned to an antiphase tilting of the oxygen octahedra. The presence of reflections with (EEO, EOE, and OEE) combinations is associated with antiparallel displacement of A-site cations. The tilting mechanism defined by the present combination of distortions is consistent with an orthorhombic a−a−c+ tilt system [11–14].

The SEM photographs of $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics sintered at 1375 °C for different x value are illustrated in Fig. 2. For all compositions, low level porosity ceramic could be observed. The grain size was increased as increasing the $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ content.

The apparent densities of the sintered bodies, with respect to the sintering temperature, are demonstrated in Fig. 3 It indicated that densities of 4.3–5.87 g/cm^3 were obtained for B_2O_3-doped $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics at sintering temperatures from 1300 °C to 1400 °C. The density increased with increasing sintering temperature due to enlarged grain size, and was also affected by the composition and decreased with increasing x value. It suggested that more $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ content and sintering at higher temperatures (above 1375 °C owing to the over-sintering) would degrade the bulk density of the ceramics.

The dielectric properties of $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ with 1 wt.% B_2O_3 addition are illustrated in Fig. 4. As the x value increased from 0.4 to 0.9, the dielectric constants decreased from 49 to 25. The dielectric constants slightly decreased with increasing sintering temperature. The decrease of ε_r value with increasing sintering temperature above 1375 °C could be explained owing to the over-sintering of $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$. With 1 wt.% B_2O_3 addition, a ε_r value of 49 was obtained for $0.4\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$0.6\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics sintered at 1375 °C.

Fig. 5 shows the $Q \times f$ values of $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-\mathrm{x})\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics with 1 wt.% B_2O_3 additions at different sintering temperatures as functions of the x value and with different x value had a maximum value at 1375 °C. The $Q \times f$ value increase with the increase of $\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$ content and sintering temperature. It was expected since that the quality factor of $\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$ is much higher than that of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ 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 $x\mathrm{Nd}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$–$(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics system was dominated by the bulk density and the grain size.

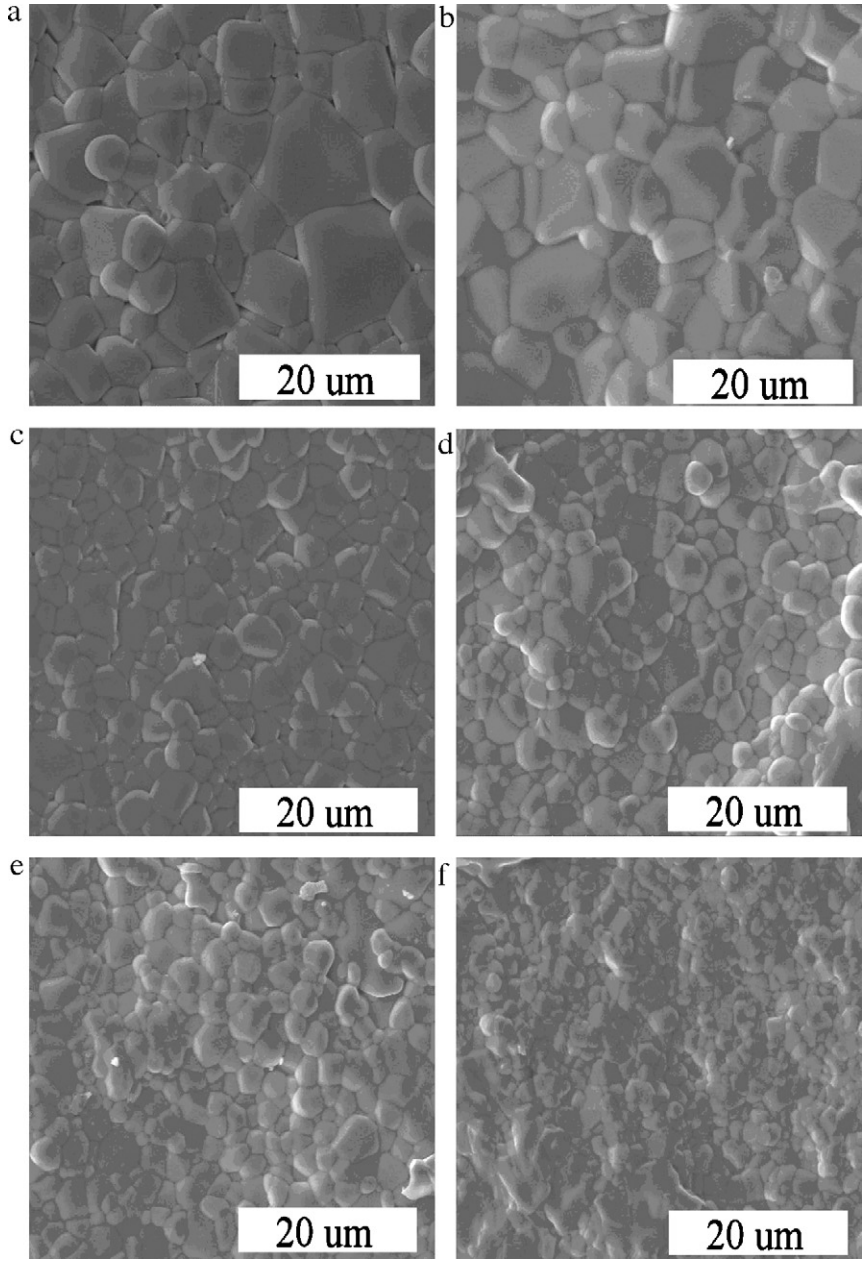

Fig. 2. SEM photographs of $x\text{Nd}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$–$(1-x)\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ ceramics (a) $x = 0.4$, (b) $x = 0.5$, (c) $x = 0.6$, (d) $x = 0.7$, (e) $x = 0.8$ and (f) $x = 0.9$ with 1 wt.% B_2O_3 additions sintered at 1375 °C for 3 h.

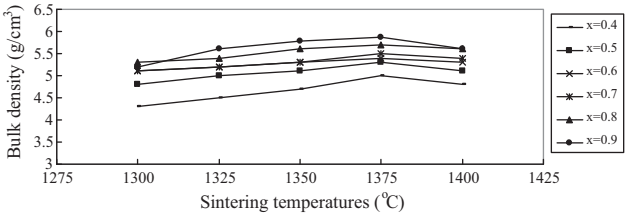

Fig. 3. Bulk density of $x\text{Nd}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$–$(1-x)\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ ceramics system sintered at different temperatures with 1 wt.% B_2O_3 addition for 3 h.

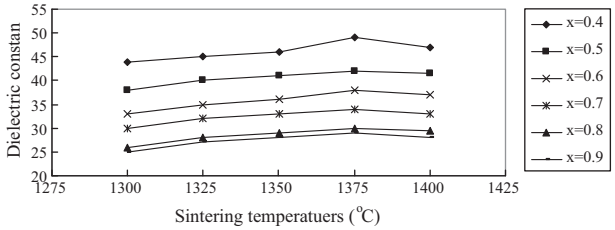

Fig. 4. ε_r value of $x\text{Nd}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$–$(1-x)\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ ceramics system sintered at different temperatures with 1 wt.% B_2O_3 addition for 3 h.

The temperature coefficients of resonant frequency (τ_f) of B_2O_3-doped $x\text{Nd}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$–$(1-x)\,\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ ceramics at different sintering temperatures are illustrated in Fig. 6. 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 $\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ content would shift the τ_f value to more positive. It varied from −46 to 1 ppm/°C as the amount of $\text{Ca}_{0.6}\text{La}_{0.8/3}\text{TiO}_3$ addition increased from 0.4 to 0.9 sintered at 1375 °C. In general, the temperature coefficient of resonant frequency was found to be related to the composition and the existing phase in ceramics.

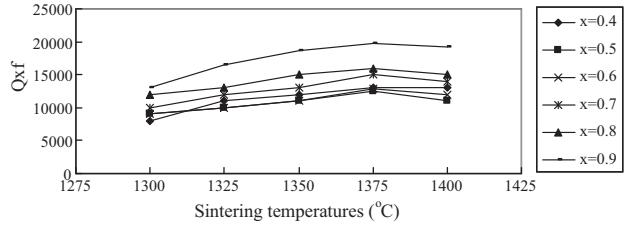

Fig. 5. $Q \times f$ value of $x\mathrm{Nd}(\mathrm{Mg_{1/2}Ti_{1/2}})\mathrm{O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics system sintered at different temperatures with various 1 wt.% B_2O_3 addition for 3 h.

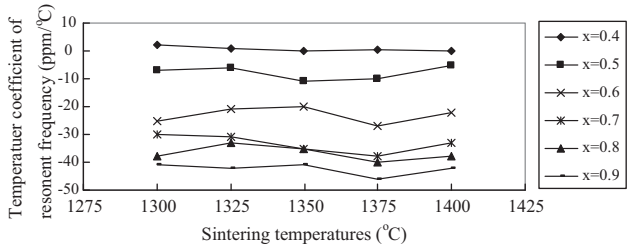

Fig. 6. Temperature coefficient value of $x\mathrm{Nd}(\mathrm{Mg_{1/2}Ti_{1/2}})\mathrm{O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics system sintered at different temperatures with 1 wt.% B_2O_3 addition for 3 h.

4. Conclusion

$x\mathrm{Nd}(\mathrm{Mg_{1/2}Ti_{1/2}})\mathrm{O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics were prepared by the solid-state route and the sintering temperature was optimized to 1375 °C for 4 h. $x\mathrm{Nd}(\mathrm{Mg_{1/2}Ti_{1/2}})\mathrm{O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics exhibited perovskite structure. With 1 wt.% B_2O_3 addition, a dielectric constant of 49, a $Q \times f$ value of 13,000 GHz and a τ_f value of 0.3 ppm/°C were obtained for $0.4\mathrm{Nd}(\mathrm{Mg_{1/2}Ti_{1/2}})\mathrm{O_3}$–$0.6\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramics at 1375 °C for 4 h. Therefore, the B_2O_3-doped $x\mathrm{Nd}(\mathrm{Mg_{1/2}Ti_{1/2}})\mathrm{O_3}$–$(1-x)\mathrm{Ca_{0.6}La_{0.8/3}TiO_3}$ ceramic is suitable for applications in microwave dielectric resonators and microwave device because of its excellent microwave dielectric properties.

Acknowledgements

This work was financially sponsored by the National Science Council of Taiwan under grant NSC-99-2221-E-309-002.

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