

# Crystallization behavior and microwave dielectric characteristics of ZnO-(La, Nd)<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-based dielectrics

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**Abstract** Crystallizable zinc borate glasses modified with different contents of La<sub>2</sub>O<sub>3</sub> or Nd<sub>2</sub>O<sub>3</sub> were investigated as a potential low loss dielectric with respect to their crystallization behavior and microwave dielectric characteristics. The glasses were admixed with Al<sub>2</sub>O<sub>3</sub> filler and fired at 850°C for 30 min in air to prepare low temperature dielectrics. Crystallization behavior and microwave dielectric properties of the resulting samples strongly depended on the relative content of La<sub>2</sub>O<sub>3</sub> or Nd<sub>2</sub>O<sub>3</sub> in the glass. As a promising result, the composition of 0.15ZnO-0.25Nd<sub>2</sub>O<sub>3</sub>-0.6B<sub>2</sub>O<sub>3</sub> exhibited  $k \sim 6.5$  and  $Q \sim 1194$  at the resonant frequency of 18.9 GHz. Near zero temperature coefficient of frequency (TCF) was obtained by additional modification of the composition with  $\sim 10$  wt.% of TiO<sub>2</sub> filler. Crystallization kinetics of the samples was studied based on the differential thermal analysis (DTA) curves obtained with different heating rates. Correlation of the observed dielectric properties to the crystallization behavior is the main subject of this work.

**Keywords** Dielectric · Glass · LTCC · Borate

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## 1 Introduction

The low temperature co-fired ceramics (LTCC) technology has been intensively studied for various electronic modules and devices requiring highly integrated packaging. The LTCC technology offers the possibility of the monolithic multilayer structures with buried passive components as a key development for integrated electronic components including IC packaging radar and antennas [1–3]. As an LTCC substrate material, dielectric ceramics have been investigated to meet the target characteristics such as low dielectric constant and high quality factor [4–6]. Zero TCF has been additionally required to get temperature stability against a frequency drift.

In recent, our previous research introduced a new LTCC material system based on a La<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass, which possesses the noticeable dielectric performance of  $k \sim 8.4$  and  $Q \sim 785$  [7]. The effect of divalent elements such as Ca, Mg, and Zn in the La<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass-based materials was studied with focusing on crystallization and its relation to the dielectric performance. As a promising result, the 0.2ZnO-0.2La<sub>2</sub>O<sub>3</sub>-0.6B<sub>2</sub>O<sub>3</sub> glass sample sintered at 850°C showed an improved  $Q$  factor of  $\sim 1091$  as related to unexpected crystallization of the ZnAl<sub>2</sub>O<sub>4</sub> and La(BO<sub>2</sub>)<sub>3</sub> phases [8]. In this continuing work, the influences of (1) glass composition modified with different contents of lanthanides such as La and Nd, and (2) TiO<sub>2</sub> filler as a partial substitute were investigated to pursue the further improvement of the dielectric performance. Crystallization behavior and phase relation to the dielectric performance are discussed with experimental evidences.

## 2 Experimental procedure

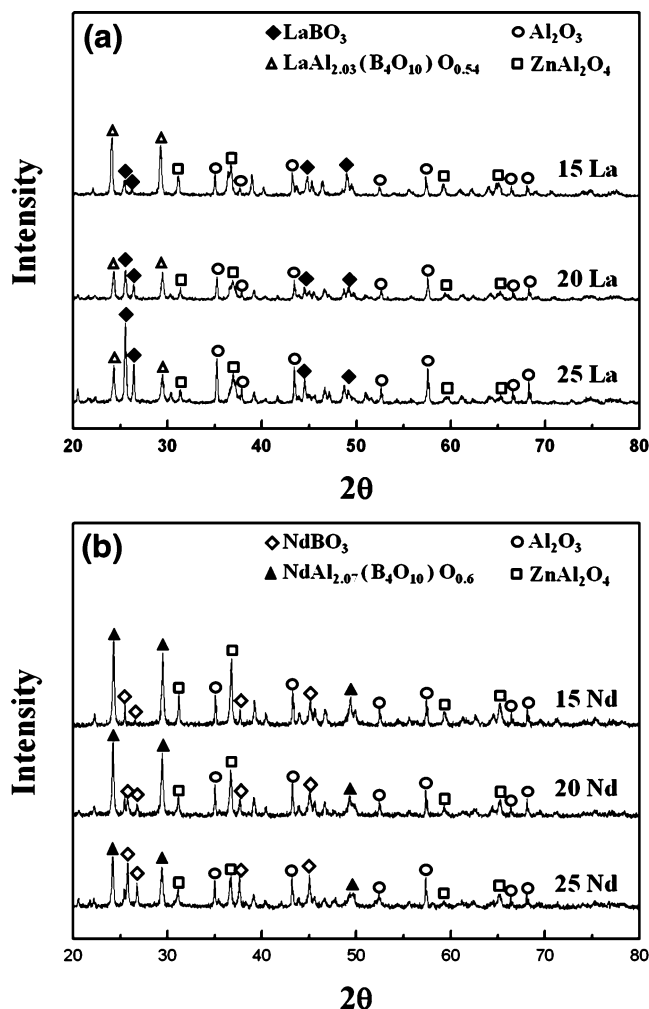
The glasses based on  $(0.4-x)\text{ZnO}-x(\text{La}, \text{Nd})_2\text{O}_3-0.6\text{B}_2\text{O}_3$  were prepared by the typical glass melting/quenching process. As the glass composition indicates, the content of  $\text{B}_2\text{O}_3$  was fixed as 0.6 molar ratio and the content ( $x$ ) of La or Nd relative to ZnO varied as  $x=0.15, 0.2$  and  $0.25$ . The sample ID was designated according to the content of La or Nd in glass. For example, “15La” indicates the glass composition of  $0.25\text{ZnO}-0.15\text{La}_2\text{O}_3-0.6\text{B}_2\text{O}_3$ . Raw materials of ZnO (99.9%, Aldrich),  $\text{B}_2\text{O}_3$  (99.9%, Kojundo Chem. Laboratory Co., Ltd.),  $\text{La}_2\text{O}_3$  (99.9% purity, Aldrich), and  $\text{Nd}_2\text{O}_3$  (>99% Terio Corporation), was mixed by hand-shacking, and melted in an uncovered platinum crucible at different soaking temperatures of  $1150^\circ$  to  $1500^\circ\text{C}$ . Each melt was quenched into a water bath to ensure a homogenous glass, ball-milled using yttria-stabilized zirconia balls for 20 h, and then dried completely at  $120^\circ\text{C}$  in an oven.

As a next step, a fixed amount of 50 wt%  $\text{Al}_2\text{O}_3$  (99.9%, Sumitomo Chemical Co., Ltd.) powder as a filler (relative to 50 wt% glass frit) was admixed with each glass frit by ball-milling in ethanol for ~6 h.  $\text{TiO}_2$  (>99%, Duksan Co.) as an additional filler was used to partially substitute the  $\text{Al}_2\text{O}_3$  filler. The glass/filler mixtures were mixed with an 1.5 wt% PVA (poly vinyl alcohol) binder solution and then pressed uniaxially at ~80 MPa to form pellets. The pellets were fired at  $450^\circ\text{C}$  for 1 h for binder removal and sintered at  $850^\circ\text{C}$  for 30 min with a heating rate of  $5^\circ\text{C}/\text{min}$  in ambient atmosphere.

Phase identification of sintered pellets was performed by using an X-ray diffractometer (Rigaku B/Max-2500/PC) with Cu  $K\alpha$  radiation having a wavelength of  $1.54 \text{ \AA}$ . Surface microstructure was examined using scanning electron microscopy (SEM: Model S-4200, Hitachi). Crystallization behavior was investigated by differential thermal analysis (DTA: Model TG/DTA-92, SETRAM) with differential heating rates (2, 3, 5, and  $7^\circ\text{C}/\text{min}$ ). Densification behavior was observed by thermo mechanical analysis (TMA) using a dilatometer (Dilatonic Tokyo Industry). Microwave dielectric properties of the sintered samples were measured with a network analyzer (Agilent 8720ES) in  $S_{21}$  transmission mode by the Hakki-Coleman dielectric resonator method [9]. The temperature coefficient of resonance frequency (TCF) was measured from  $25^\circ$  to  $70^\circ\text{C}$  in a chamber.

## 3 Results and discussion

Figure 1 shows the XRD patterns of the samples containing different La and Nd contents in glass. All samples containing La had three distinct crystalline phases of

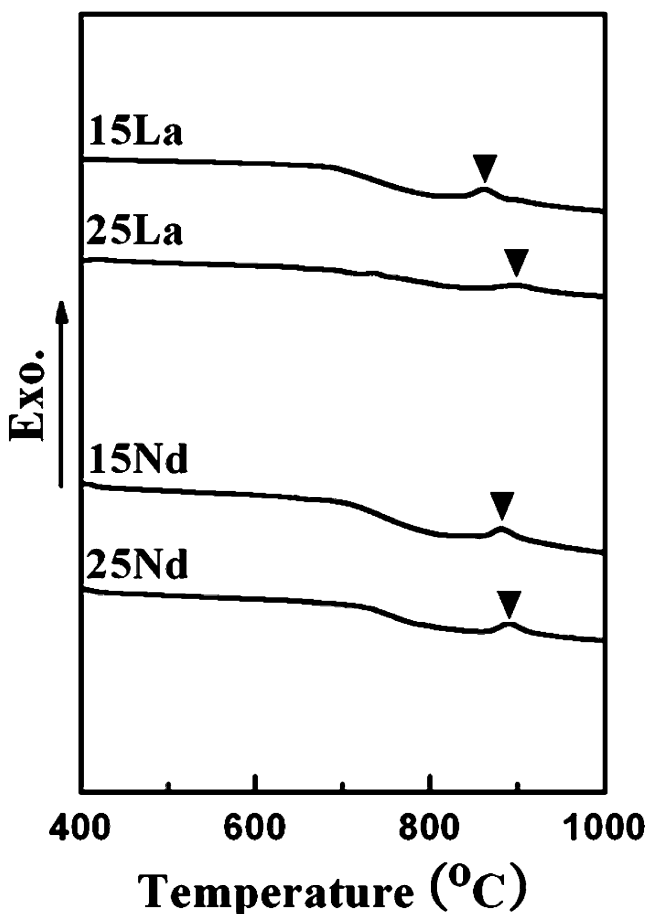


**Fig. 1** X-ray diffraction patterns of the (a) La- and (b) Nd-glass samples fired at  $850^\circ\text{C}$

$\text{LaBO}_3$ ,  $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$  and  $\text{ZnAl}_2\text{O}_4$  regardless of the content of La as a result of the  $850^\circ\text{C}$  firing. Similarly, the Nd-containing samples showed crystalline phases of  $\text{NdBO}_3$ ,  $\text{NdAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$  and  $\text{ZnAl}_2\text{O}_4$  as major phases. The relative peak intensities were dependent on the La or Nd content. For example, the peak intensities of  $\text{LaBO}_3$  phase increased obviously relative to those of  $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$  phase as compared in the  $2\theta$  range of  $24$  to  $30^\circ$  in Fig. 1(a). It indicates that  $\text{LaBO}_3$  phase becomes more dominant with increasing the La content in glass. As an accompanying result, the relative peak intensities of  $\text{ZnAl}_2\text{O}_4$  decreased with increasing the La content in glass. Nd-containing samples showed the similar behavior of the phase evolution as that of La-containing samples. The peak intensities of  $\text{NdBO}_3$  phase increased while those of  $\text{NdAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$  phase decreased gradually with increasing the Nd content in the glass.

Figure 2 shows the DTA curves of the samples containing 50 wt%  $\text{Al}_2\text{O}_3$  filler with varying the content of La and Nd. The softening points ( $T_{\text{softening}}$ ) obtained

from the DTA curves are represented in Table 1 with other physical properties of the samples. The softening point tends to shift toward a higher temperature as the content of La or Nd increased. In the case of the Nd glass, this effect was more prominent as evidenced with the 20°C difference between the 15Nd and 25Nd glasses. This shift may be reasonable when considered the potential contribution of more Zn (lesser La or Nd) to the easier softening of glass. The position of crystallization peaks, as indicated as arrows in Fig. 2, also seemed to be sensitive to the content of La or Nd. The samples with more La or Nd tend to exhibit crystallization peaks at higher temperatures. It should be mentioned that it was not easy to find distinguishable crystallization peaks that could be matched with phases observed in the XRD patterns of Fig. 1 probably due to the overlapped crystallizations peaks and/or the less sensitivity of the DTA instruments. It may be reasonably assumed, however, that the crystallization peak indicated by the arrow corresponds to the  $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$  or  $\text{NdAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$  phase since the relative peak intensities of the phase tended to decrease with more La or Nd content.



**Fig. 2** DTA curves of the La- and Nd-glass samples containing 50 wt%  $\text{Al}_2\text{O}_3$

**Table 1** Physical properties of the samples containing 50 wt%  $\text{Al}_2\text{O}_3$  with different contents of La and Nd elements.

Composition (mol%)		$T_{\text{softening}}$ (°C)	$T_{\text{densification onset}}$ (°C)	Fired density ( $\text{g}/\text{Cm}^3$ )	$x$ - $y$ shrinkage (%)
ZnO	$\text{La}_2\text{O}_3$				
25	15	3.59	638	3.59	14.8
*20	20	3.39	650	3.39	11.0
15	25	2.76	658	2.76	5.8
ZnO	$\text{Nd}_2\text{O}_3$				
25	15	3.57	645	3.57	12.7
20	20	3.65	649	3.65	13.8
15	25	3.13	673	3.13	8.2

\*Ref [8]

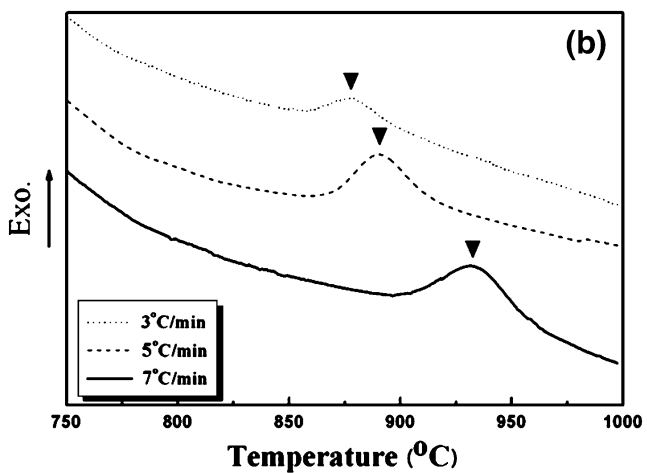
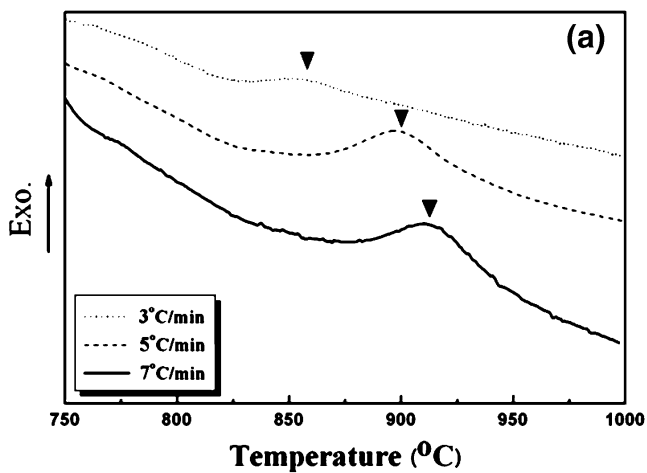
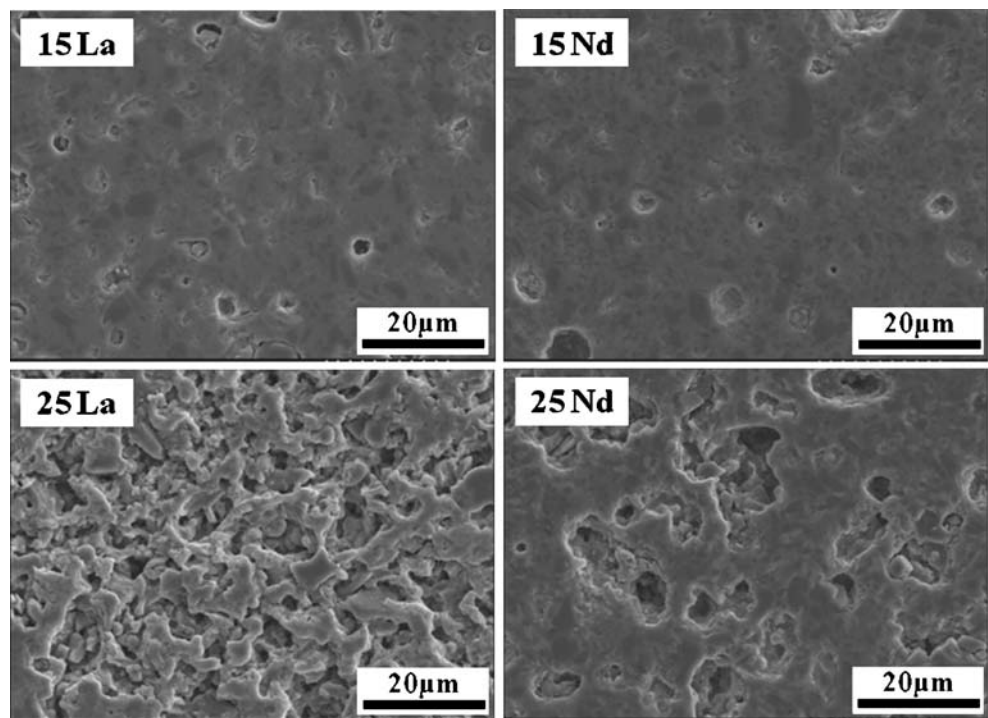
Other physical properties such as fired density and  $x$ - $y$  shrinkage also depended on the glass composition as shown in Table 1. It was believed that the appropriate content of Zn in glass was needed for the enhanced densification. This correlation of densification to the content of Zn in glass agreed well with the surface microstructures of the samples as shown in Fig. 3. The samples with higher contents of La and Nd clearly displayed porous surfaces. The result must be associated with observed higher softening points of the glasses containing more La or Nd. Variations in the densification onset temperature ( $T_{\text{densification onset}}$ ) obtained from the TMA curves in Table 1 also supported the tendency that the high content of La or Nd seemed less capable of earlier densification.

The crystallization kinetics was studied by changing the heating rate from 2° to 7°C/min during the DTA measurement. Figure 4 showed the DTA curves obtained for the 25La and 25Nd samples at different heating rates. The exothermic crystallization peak position distinctively shifted toward the lower temperature region with accompanying the peak broadening as the DTA heating rate decreased. The change with heating rate is expected when considered other DTA studies concerning the crystallization behavior of common glasses [10–12]. The changes of peak position with different heating rates were used to calculate activation energy for crystallization by using the known Kissinger method [13]. The following equation was used to calculate the activation energy for crystallization [14].

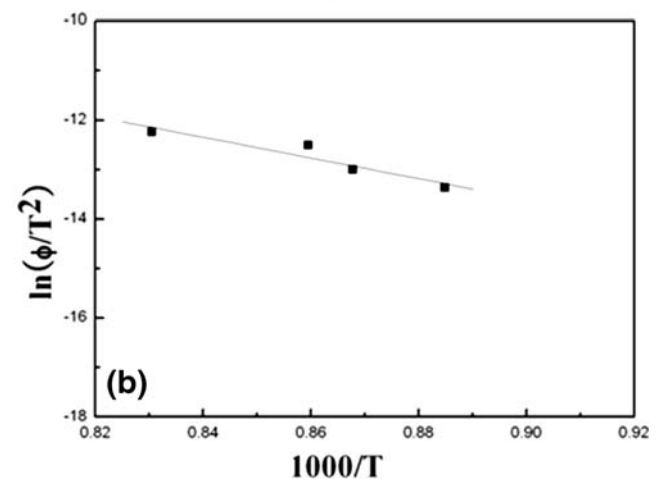
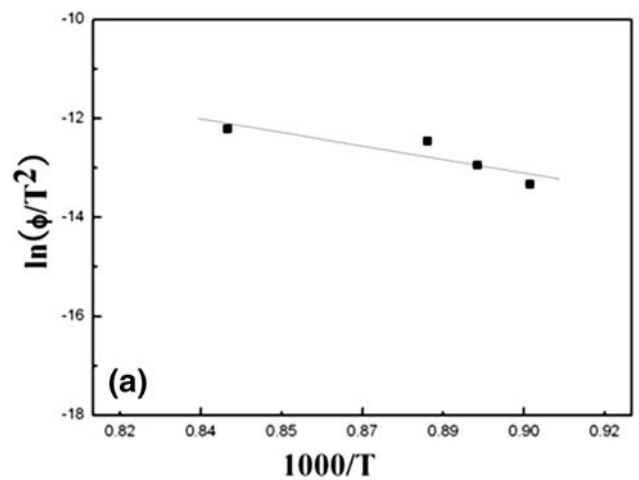
$$\ln(\Phi/T^2) = -E_c/RT + \text{constant} \quad (1)$$

where  $\Phi$  is the heating rate of DTA,  $T$  is the crystallization peak temperature,  $E_c$  is the activation energy for crystallization, and  $R$  is the gas constant. The slope of these straight plots indicated the activation energy for crystallization. Figure 5 represents the plots of  $\ln(\Phi/T^2)$  vs  $1/T$  for the 25La and 25Nd samples. The activation energy of the two

**Fig. 3** SEM microstructures of the 15La, 25La, 15Nd and 25Nd samples fired at 850°C



**Fig. 4** DTA curves of the (a) 25La and (b) 25Nd samples, obtained at different heating rates of 3, 5 and 7°C/min



**Fig. 5** Plots of  $\ln(\Phi/T^2)$  versus  $1/T$  for the (a) 25La and (b) 25Nd samples

**Table 2** Dielectric properties of the samples containing 50 wt% Al<sub>2</sub>O<sub>3</sub> with different contents of La and Nd elements.

Composition (mol%)		Resonance frequency (GHz)	Dielectric constant ( <i>k</i> )	Quality factor ( <i>Q</i> )	<i>Q</i> × <i>f</i>
ZnO	La <sub>2</sub> O <sub>3</sub>				
25	15	18.0	8.0	793	14,274
*20	20	18.3	7.4	890	16,230
15	25	17.7	7.6	960	16,992
ZnO Nd <sub>2</sub> O <sub>3</sub>					
25	15	19.6	7.4	762	14,935
20	20	17.8	7.8	863	15,361
15	25	18.9	6.5	1,194	22,567

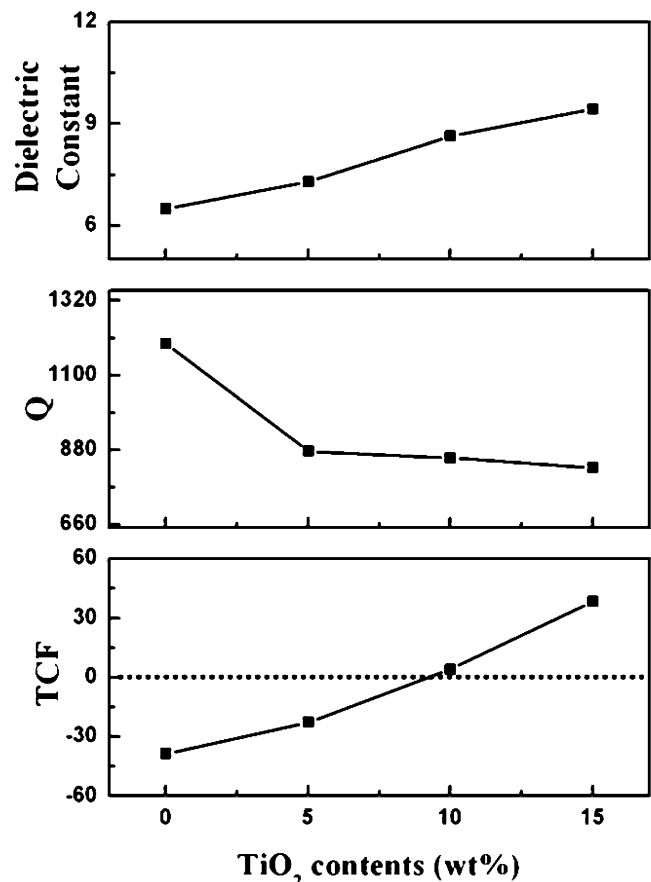
\* Ref [8]

samples was calculated as 39.8 and 41.1 kcal/mol, respectively, which are higher than a reported value of ~13.7 kcal/mol for lead borate glasses [10, 15]. It may be concluded from the similar activation energies for the 25La and 25Nd samples that a very comparable energy is required for the crystallization of rare earth-containing glass system.

Dielectric properties measured in the resonant frequency range of 18.0–19.6 GHz were summarized in Table 2. The overall dielectric constant ranged from 6.5 to 8.0 regardless of dielectric composition. The higher porosity observed with more La and Nd is likely responsible for lower dielectric constants of the 25La and 25Nd samples. Quality factor seemed to be more sensitive to the composition. Increasing the content of La or Nd tends to produce higher *Q* factors. For instance, quality factor of the La samples increased from 793 to 960 as increasing the La content in glass. This observation is interesting when considered a higher porosity with more La or Nd because poor porosity generally leads to the degradation of quality factor. A possible explanation for high *Q* values for more La or Nd may be coming from the crystalline phases developed depending on the relative content of La or Nd to Zn in glass. It was assumed in our previous study on the dielectrics of RO-La<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> (R=Ca, Mg and Zn), that potential crystalline phases including LaBO<sub>3</sub> and ZnAl<sub>2</sub>O<sub>4</sub> are responsible for the unusual high *Q* values [7, 8]. Similarly, the phases of LaBO<sub>3</sub> and NdBO<sub>3</sub>, which were found more dominantly with more La and Nd in Fig. 1, are thought to be directly related to the enhanced quality factors. The highest quality factor of 1194 was achieved for the 25Nd sample, which was a significant improvement when considered typical *Q* values of <400 for common LTCC materials.

Additional efforts were made to improve negative TCF values of ranging from -40 ppm/°C to -10 ppm/°C regardless of glass composition. The 25Nd sample having

the highest *Q* of 1194 and a TCF of -38 ppm/°C was selected to study the effect of the addition of TiO<sub>2</sub> filler having a positive TCF. Figure 6 shows the dielectric properties of the 850°C samples when TiO<sub>2</sub> was partially used as a filler. The content of TiO<sub>2</sub> in the *x*-axis corresponds to weight percentage of TiO<sub>2</sub> substituted in the 50 wt% alumina filler. For example, 5 wt% TiO<sub>2</sub> indicates that the filler consists of 5 wt% TiO<sub>2</sub> and 45 wt% Al<sub>2</sub>O<sub>3</sub>. As expected from the reported TCF~+450 ppm/°C and *k*~120 of TiO<sub>2</sub>, TCF tended to increase toward the positive values and dielectric constant gradually increased with TiO<sub>2</sub> filler [16]. Near zero TCF could be obtained when 10 wt% TiO<sub>2</sub> was added. It is known that the TCF value is determined by the mixing rule among the co-existing phases [17]. It is difficult in this system to anticipate the final TCF values based on the mixing rule because the TCF values of each crystalline phase and uncrystallized glass are unknown. At least, however, it can be concluded that an appropriate choice of filler as well as glass composition can control the final dielectric properties. Quality factor decreased with increasing the contents of

**Fig. 6** Dielectric constant, quality factor and TCF as a function of TiO<sub>2</sub> content for the samples containing the 25Nd glass



TiO<sub>2</sub> powder and a drastic decrement was found up to the level of 5 wt% of the TiO<sub>2</sub> filler.

#### 4 Conclusions

The crystallization behavior and microwave dielectric properties of the LTCC systems consisting of (0.4-x)ZnO-x(La,Nd)<sub>2</sub>O<sub>3</sub>-0.6B<sub>2</sub>O<sub>3</sub> (x=0.15, 0.2 and 0.25) glass and Al<sub>2</sub>O<sub>3</sub> filler were investigated at the low sintering temperature of 850°C. Phase development and densification depended strongly on the relative content of La or Nd. Based on the experimental evidences, it was assumed that phase development, rather than porosity of the samples, had a stronger influence on quality factor in the lanthanide glass system. Among all the samples, particularly, the 0.15ZnO-0.25Nd<sub>2</sub>O<sub>3</sub>-0.6B<sub>2</sub>O<sub>3</sub> glass sample showed the lowest dielectric constant and the highest quality factor of 6.5 and 1194 at 18.9 GHz, respectively. Crystalline phases such as LaBO<sub>3</sub> and NdBO<sub>3</sub>, which become more predominant with more La or Nd in glass, are thought to be responsible for the improved Q factor. The partial substitution of alumina filler with TiO<sub>2</sub> is proven to be beneficial in producing near zero TCF from the negative values of the glass samples.

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