Journal of Alloys and Compounds 509 (2011) 849–853

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Effect of Zn and Ca modifications on crystallization and microwave dielectric properties of lanthanum borates

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ARTICLE INFO

Article history:
Received 16 August 2010
Received in revised form
10 September 2010
Accepted 19 September 2010
Available online 29 September 2010

Keywords:
Lanthanum borates
Microwave dielectrics
Crystallization
Glass–ceramic

ABSTRACT

Low loss dielectrics based on two borate glasses, (13–19)CaO·(13–19)La_2O_3·68B_2O_3 and (13–19)ZnO·(13–19)La_2O_3·68B_2O_3, have been investigated with a focus on effects of the CaO/La_2O_3 and ZnO/La_2O_3 ratios on physical and dielectric properties. All samples were prepared by mixing glass with 40 wt% Al_2O_3 filler and by firing at 850 °C for 30 min. The effects of increasing relative contents of Ca and Zn were found to be opposite specifically in microstructure evolution and crystallization behavior, and thus, dielectric properties. For example, the 13CaO·19La_2O_3·B_2O_3 sample having the lowest Ca content showed the highest $Q \times f$ of ~8100, while the 19ZnO·13La_2O_3·B_2O_3 sample having the highest Zn content showed the highest $Q \times f$ of ~18,100. The extensive crystallization of low loss phases, i.e., $LaBO_3$ and $LaAl_{2.03}(B_4O_{10})O_{0.54}$, as well as the improved level of densification are assumed to be responsible for better dielectric performance.

1. Introduction

Multilayer ceramic substrates have been widely used in commercial electronic modules and devices requiring highly integrated packaging within a limited volume. The low temperature co-fired ceramics (LTCC) technology has been one of the competitive solutions that can satisfy high signal-transmission speed, high wiring density, high volumetric efficiency, excellent reliability, and low production cost [1–4]. Furthermore, passive components (such as capacitors and inductors) can be embedded into the LTCC substrates, and co-fired with low cost metals (such as silver and copper) below 950 °C. For the best utilization as a substrate, LTCC materials should have low dielectric constant, high quality factor, high mechanical strength, and high thermal conductivity [5,6]. Complete densification and desirable crystallization must be achieved at relatively low sintering temperatures for reliable dielectric, thermal and mechanical properties.

In order to reduce sintering temperature, the intimate combination of glass and ceramic filler has been usually used. Particularly, the softening temperature (T_s) of glass plays an important role in reducing sintering temperature. Our previous research introduced a new LTCC material system based on the glass of La_2O_3–B_2O_3, which aims particularly for very high quality factors greater than 1000 for millimeter wave applications operating at >10 GHz [7–9]. Modified LTCC material systems based on RO·La_2O_3·B_2O_3 (R = Ca, Mg and Zn) glasses have been proven to have better dielectric properties. As a promising example, 27ZnO·16La_2O_3·57B_2O_3 glass showed desirable performance of $k \sim 7.8$ and $Q \sim 1350$ at 16.8 GHz when sintered at 950 °C with 50 wt% Al_2O_3 filler [9].

This work deals with further manipulation of two relevant glasses, CaO·La_2O_3·B_2O_3 and ZnO·La_2O_3·B_2O_3, by changing the ratios of CaO/La_2O_3 and ZnO/La_2O_3. Crystallization, densification and microstructures of the resultant samples have been correlated to microwave dielectric properties obtained at >10 GHz.

2. Experimental procedure

Two glass series of (13–19)CaO·(13–19)La_2O_3·68B_2O_3 and (13–19)ZnO·(13–19)La_2O_3·68B_2O_3 in mol% were used in this study. Note that the content of B_2O_3 was fixed at 68 mol%. Raw materials, CaO (99.9% purity, Aldrich, Milwaukee, WI), ZnO (99.9% purity, Aldrich, Milwaukee, WI), La_2O_3 (99.9% purity, Aldrich, Milwaukee, WI) and B_2O_3 (99.9% purity, Kojundo Chemical Lab. Co., Ltd., Tokyo, Japan), were mixed by hand-shaking for 5 min and melted in an uncovered Pt crucible at 1200 °C for 1 h. The melt was quickly quenched into a roller quencher, ball-milled with yttria-stabilized zirconia balls in alcohol for about 20 h, and then dried completely at 120 °C in an oven. As a next step, a fixed 40 wt% of high purity Al_2O_3 (99.9%, ALM43, Sumitomo Chemical Co., Ltd., Tokyo, Japan) powder was admixed with the 60 wt% glass frit by ball milling in alcohol for 10 h. The mixture was dried at ~120 °C and pressed at ~80 MPa to form pellets of ~12 mm in diameter. The pellets were sintered at a fixed firing condition of 850 °C for 30 min in ambient atmosphere. The sample ID was designated by representing the ratio of either CaO/La_2O_3 or ZnO/La_2O_3 in glass. For example, 13Ca/19La indicates a composition consisting of 60 wt% 13CaO·19La_2O_3·68B_2O_3 glass and 40 wt% Al_2O_3 filler.

Crystalline phase developed in the sintered samples was determined by an X-ray diffractometer (Rigaku B/Max-2500/PC, Tokyo, Japan). Differential thermal analysis (DTA; Setram TG/DTA-92, Calurie, France) was performed at a heating rate of 5 °C/min to study the firing behavior. The surface of the sintered samples was exam-

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doi:10.1016/j.jallcom.2010.09.110

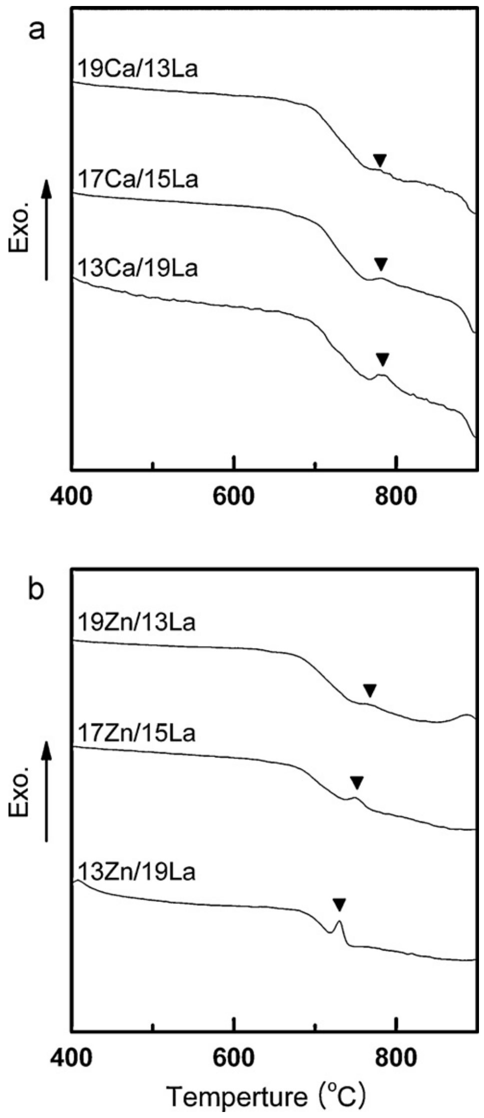

Fig. 1. DTA curves of the (a) Ca/La and (b) Zn/La samples.

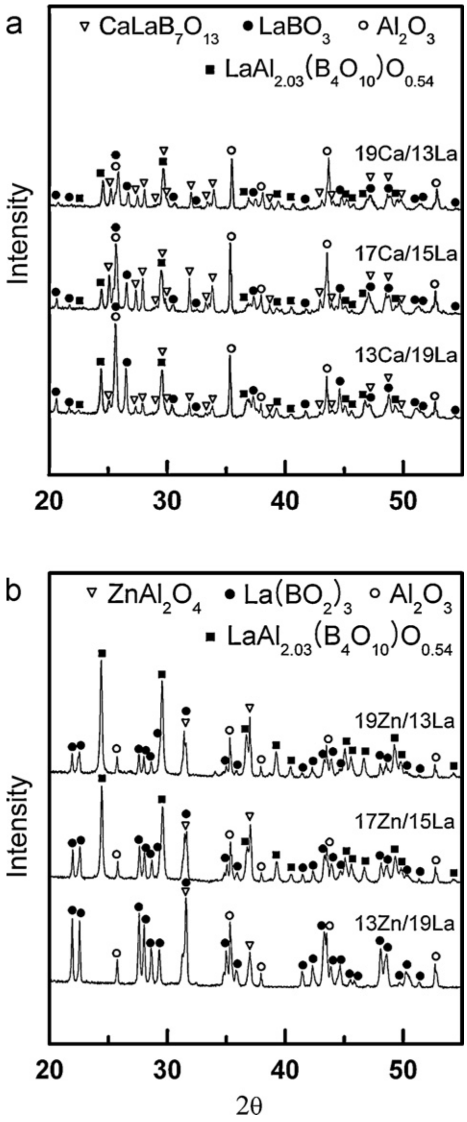

Fig. 2. X-ray diffraction patterns of the (a) Ca/La and (b) Zn/La samples fired at 850 °C.

ined by scanning electron microscopy (SEM; Hitachi S-4200, Nissei Sangyo, Japan). Density of sintered samples was measured by the Archimedes principle. Microwave dielectric properties of the sintered samples were measured using a network analyzer (Agilent 8720ES) in an S_{21} transmission mode by the Hakki–Coleman dielectric resonator method.

3. Results and discussion

Fig. 1(a) shows DTA curves of the samples based on 60 wt% CaO/ZnO·La_2O_3·B_2O_3 glass and 40 wt% Al_2O_3 filler. Table 1 represents several quantitative data including glass transition temperature (T_g), softening temperature (T_s), crystallization onset temperature ($T_{c,onset}$) and crystallization peak temperature ($T_{c,peak}$) of each composition, which are obtained from the DTA curves. The DTA curves are typically specified with softening of glass at low temperatures and then exothermic crystallization reaction (as indicated by arrows) at higher temperatures. The T_g and T_s values are dependant on the ratios of Ca/La and Zn/La. For instance, the increase of the content of Ca and Zn relative to La tends to decrease T_g and T_s, which indicates that the divalent cations soften the glass earlier. It is noticeable that Zn in glass brought much lower T_s of ~647–656 °C compared to ~678–688 °C for Ca. This is basically due to the lower dissociation energy, 144 kcal, of Zn–O compared to 257 kcal for Ca–O [10].

Table 1
Summary of DTA data obtained for the Ca/La and Zn/La samples.

Sample ID	T_g (°C)	T_s (°C)	$T_{c,onset}$ (°C)	$T_{c,peak}$ (°C)	$\Delta(T_{c,onset} - T_s)$ (°C)
13Ca/19La	658	688	760	786	72
17Ca/15La	656	680	757	783	77
19Ca/13La	655	678	756	782	78
13Zn/19La	641	656	712	729	56
17Zn/15La	629	649	730	750	81
19Zn/13La	622	647	741	767	94

However, the effect of the variations in the ratios of Ca/La and Zn/La on crystallization behavior appears to be different as exemplified in the $T_{c,onset}$ and $T_{c,peak}$ in Table 1. Crystallization is found to be more sensitive to the change of Zn/La than Ca/La. For example, the increase in the Ca/La ratio resulted in slight decrease in $T_{c,peak}$ from 786 to 782 °C while increasing Zn/La raised $T_{c,peak}$ significantly from ~720 to ~767 °C. In addition, the increase of the Zn/La ratio tends to broaden the temperature range of crystallization as seen in the Fig. 1(b). Note that more distinct exothermic peak in the narrower range of temperature was found in the case of 13Zn/19La that has the lowest content of Zn.

Development of the crystalline phases was studied from the analysis of the XRD patterns shown in Fig. 2. The Ca/La samples were observed to consist of crystalline phases, $LaBO_3$, $LaAl_{2.03}(B_4O_{10})O_{0.54}$ and $CaLaB_7O_{13}$, along with Al_2O_3 phase added as a filler (Fig. 2(a)). In the case of Zn/La samples, the crystalline phases of $LaAl_{2.03}(B_4O_{10})O_{0.54}$, $ZnAl_2O_4$ and $La(BO_2)_3$ were found. These phases were believed to be crystallized over the temperature range above 700 °C, which was defined from the DTA exothermic peaks of Fig. 1, depending on each glass composition. As reported previously in the study of similar glasses, it is very hard to find separate exothermic peak of each phase in the DTA curve [8]. It is apparent that Ca and Zn are involved in the crystallization process by forming $CaLaB_7O_{13}$ and $ZnAl_2O_4$, respectively. As a common phase in both glass systems, $LaAl_{2.03}(B_4O_{10})O_{0.54}$ was observed.

Relative contents of each crystalline phase with increasing the ratios of Ca/La and Zn/La were quantitatively expressed by comparing the highest intensity peak of each phase relative to the summation of the strongest intensities of all existing crystalline phases as shown in Fig. 3. For example, the relative content of $ZnAl_2O_4$ for the Zn/La samples was obtained by the following equation,

$$\text{Relative content of } ZnAl_2O_4 = \frac{I_{ZnAl_2O_4}}{I_{ZnAl_2O_4} + I_{La(BO_2)_3} + I_{LaAl_{2.03}(B_4O_{10})O_{0.54}} + I_{Al_2O_3}}$$

where $I_{ZnAl2O4}$ is the intensity of the strongest (3 1 1) peak of the $ZnAl_2O_4$ phase. These curves clearly indicate that the relative content of each phase depends differently on the ratios of Ca/La and Zn/La. The degree of overall dependence of the phase evolution is more significant in the Zn/La samples than in the Ca/La samples. In the Ca/La samples, an increase of $CaLaB_7O_{13}$ is observed with increasing Ca, which reasonably indicates that Ca in the glass is involved in crystallization more progressively as the relative content of Ca increases. In the meanwhile, it is observed that the relative content of $LaBO_3$ decreases distinctively with increasing Ca (thus decreasing La).

In the case of Zn/La samples, it is distinguishable that the relative content of Al_2O_3 filler is significantly reduced with increasing

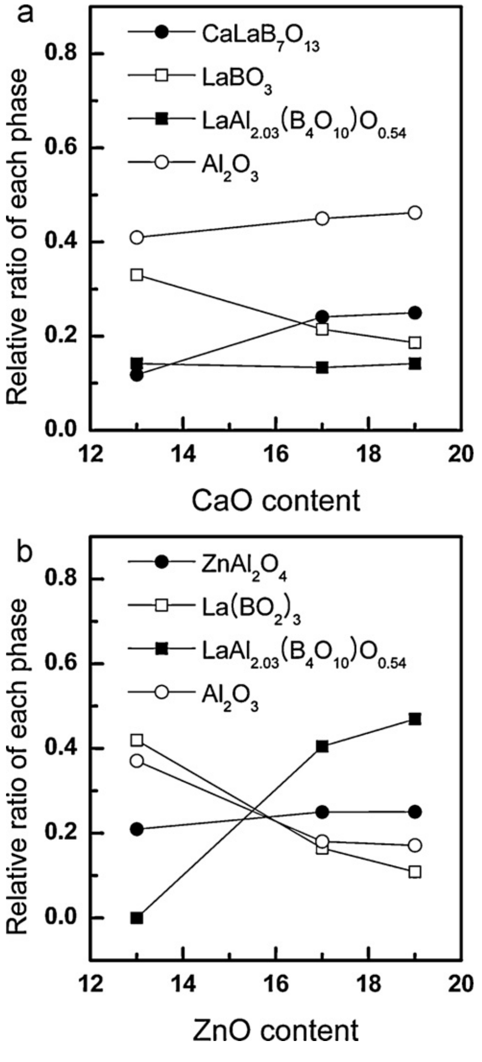

Fig. 3. Variations of relative content of each crystalline phase with increasing CaO or ZnO for the (a) Ca/La and (b) Zn/La samples fired at 850 °C.

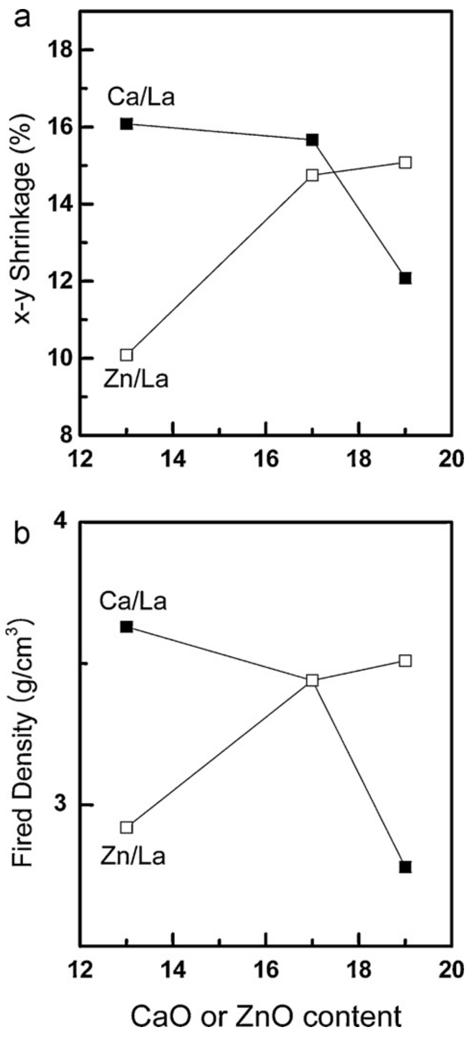

Fig. 4. Variations of (a) x–y shrinkage and (b) fired density with increasing CaO or ZnO for the Ca/La and Zn/La samples.

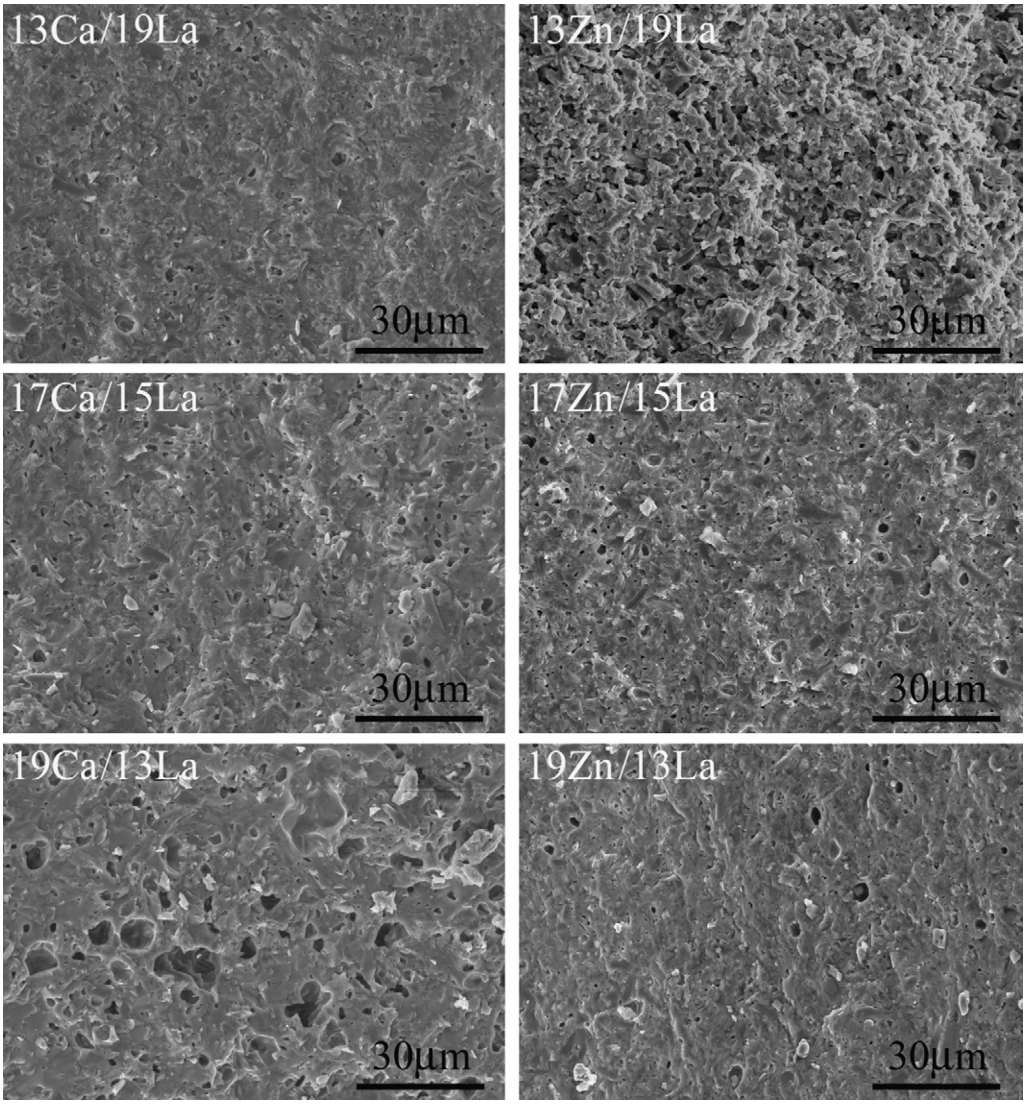

Fig. 5. Microstructures of fracture surfaces of the Ca/La and Zn/La samples fired at 850 °C.

Zn content. It seems that Al_2O_3 becomes more associated with crystallization of the Al-containing phases such as $ZnAl_2O_4$ and $LaAl_{2.03}(B_4O_{10})O_{0.54}$ with increasing content of Zn. The phase of $LaAl_{2.03}(B_4O_{10})O_{0.54}$ changed most significantly with increasing Zn. Note, in the Ca/La samples, that the $LaAl_{2.03}(B_4O_{10})O_{0.54}$ phase was not much developed with increasing Ca while the relative content of Al_2O_3 increased marginally.

Fig. 4 represents the *x*–*y* shrinkage and fired density of the samples after firing at 850 °C. The results of the Ca/La and Zn/La cases were opposite. Both shrinkage and fired density values were found to decrease with increasing relative content of Ca and exhibit an inverse trend for the Zn content. Fig. 5 shows the fracture surfaces of the corresponding samples. Microstructural characteristics match well with the tendency of shrinkage and density variations in each case. The samples having the lowest content of Ca or the highest content of Zn showed the best characteristics of microstructure, i.e., least porosity. As expected, the microstructure was found to consist of various crystalline phases that are well dispersed in the glass matrix.

Generally, the degree of densification depends on the softening temperature of glass in a composite of glass and refractory ceramic [11]. Earlier softening of glass is preferred for full densification as lower temperatures. When glass participates actively in crystallization during firing, however, densification is influenced depending on the temperature of crystallization. Earlier densification prior to extensive crystallization is typically preferred since densification is difficult to proceed once significant crystallization happens.

Accordingly, separation between densification and crystallization temperatures can be critical in generating desirable microstructure without macro-pores. In this regard, the temperature difference $\Delta(T_{c,onset} - T_s)$ between T_s and $T_{c,onset}$ for each composition is listed in Table 1. For example, the 19Zn/13La samples having the largest $\Delta(T_{c,onset} - T_s)$ of 94 °C must be the ideal case as confirmed in the enhanced densification and microstructure. The Zn/La samples tend to have higher density and better microstructure with increasing Zn, which can be correlated with lowered T_s and raised $T_{c,onset}$. As a result, the 19Zn/13La samples exhibited the highest fired density of 3.51 g/cm^3 with an *x*–*y* linear shrinkage of 15.1%. On the other hand, the 19Ca/13La sample having the highest content of Ca showed the lowest density value even with the lowest softening temperature. Earlier crystallization with more Ca might hinder densification of the samples.

Microwave dielectric properties, dielectric constant and $Q \times f$, measured in the resonant frequency range of 16.2–18.9 GHz are shown in Fig. 6. Dielectric constants ranged from 6.1 to 8.5 for the Ca/La and Zn/La samples, which are comparable to 6.5–9 values

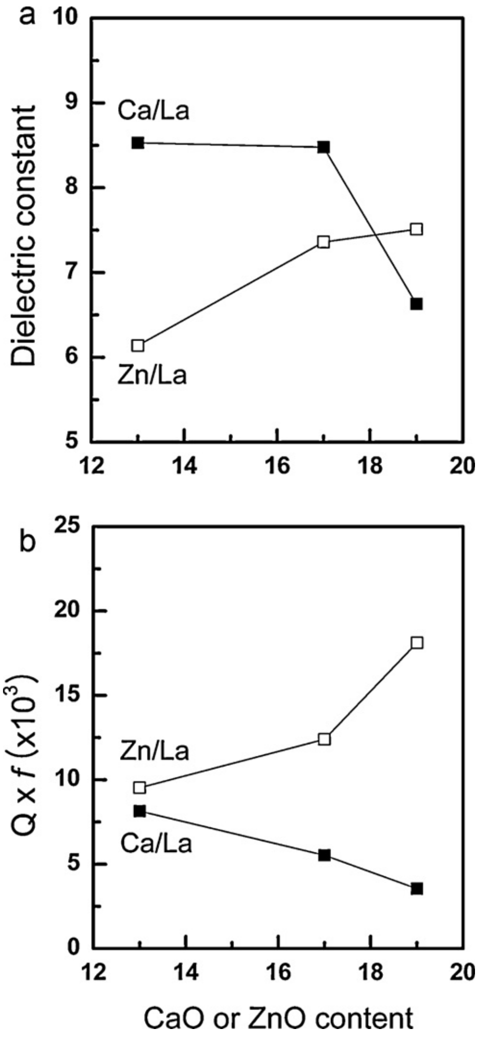

Fig. 6. Variations of (a) dielectric constant and (b) $Q \times f$ with increasing CaO or ZnO for the Ca/La and Zn/La samples.

reported for commercial LTCC materials [8,12,13]. The dielectric parameters strongly depended on the relative content of Ca and Zn in glass, as expected. The varying tendencies agree well with the results of densification and microstructures resulted by different Ca or Zn contents. For example, the 19Zn/13La sample that has the highest Zn content as well as the highest density and least porosity demonstrates a higher dielectric constant of ~7.4 and a higher $Q \times f$ of ~18,100. In the Ca/La case, however, increasing the content of Ca tends to decrease dielectric constant and quality factor. The 13CaO·19La_2O_3·B_2O_3 sample having the lowest Ca content had better $Q \times f$ of ~8100, compared to the other Ca-containing samples.

In addition to the correlation of dielectric parameters to the degree of densification, crystalline phases developed during firing must be considered as critical factors in influencing the final dielectric performance. In this similar material system of lanthanum borates, the existence of $LaBO_3$, $LaAl_{2.03}(B_4O_{10})O_{0.54}$ and $ZnAl_2O_4$ phases has been analyzed as responsible for enhanced quality factor [7,8]. As demonstrated earlier in Fig. 3, the level of each crystalline phase strongly depends on the content of Ca or Zn relative to La. It is apparent in the Zn/La samples, as an example, that the dominance of the $LaAl_{2.03}(B_4O_{10})O_{0.54}$ phase seems to be in charge of enhanced $Q \times f$ values for the higher Zn samples. In the Ca/La samples, on the other hand, the reduced content of the $LaBO_3$ phase with increasing Ca (thus decreasing La) must be partially associated with the lowered $Q \times f$ value although poorer densification induced with increasing Ca may be a more influencing factor.

4. Conclusions

The effects of Ca and Zn modifications were different in terms of densification and microwave dielectric properties of the (13–19)CaO·(13–19)La_2O_3·68B_2O_3 and (13–19)ZnO·(13–19)La_2O_3·68B_2O_3 samples containing a fixed amount of 40 wt% Al_2O_3. The difference was based on different levels of densification and crystallization, which depend on relative contents of Ca or Zn. In the CaO·La_2O_3·B_2O_3 samples, the lower content of Ca is preferred since densification is enhanced and more $LaBO_3$ phase is produced. In the ZnO·La_2O_3·B_2O_3 samples, on the contrary, the higher content of Zn seems to be more effective in generating a larger difference between the softening and crystallization temperatures, and, hence, better densification with least porosity. As the best glass composition, 19ZnO·13La_2O_3·68B_2O_3 having the increased content of the $LaAl_{2.03}(B_4O_{10})O_{0.54}$ phase exhibited promising dielectric properties of $k \sim 7.4$ and $Q \times f$ ~18,100.

Acknowledgements

This work was supported by Korea Energy Management Corporation (KEMCO) of the Ministry of Knowledge Economy and partially, by the Defense Nano-Technology Application Center.

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