

Physical and dielectric properties of BaTiO₃–fluoride–glass systems for nitrogen-fireable embedded capacitors

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Abstract BaTiO₃-based dielectrics containing the selective additive combinations from Pb-free glasses and fluoride compounds such as AlF₃, BaF₂, CaF₂, LiF and ZnF₂ were studied mainly for a potential N₂-fireable embedded capacitor in printed circuit board with Cu metallization. The physical and dielectric properties, such as dielectric constant (k), loss tangent ($\tan\delta$) and T_c , strongly depended on the choice of additive combination. A bismuth borosilicate glass was most promising in terms of the degree of densification and dielectric constant. The samples containing LiF and ZnF₂ and sintered at 950 °C looked most beneficial in that these additives produced high k of >1,200 and low $\tan\delta$ of < 0.022 at room temperature regardless of sintering atmosphere. As an example, the 95BaTiO₃–2LiF–3(Bi borosilicate) sample exhibited $k\sim 1,340$ and $\tan\delta\sim 0.022$ at room temperature when fired at 950 °C in N₂.

Keywords Embedded capacitor · BaTiO₃ · Fluoride · Dielectrics · High k · PCB

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1 Introduction

Embedded passive components have been studied to provide a unique solution for highly-integrated electronic modules or devices [1, 2]. As an embedded capacitor in Cu-printed circuit board (PCB) substrates, specifically, thick film dielectrics with a high dielectric constant $k > 1,000$ have a great potential in fabricating high-density packages [3–7]. Due to the restricted firing condition of Cu metallization, there have been difficulties in achieving reliable physical and electrical performance of capacitive thick films on Cu foils. High k dielectrics on Cu foils had to be produced at low temperatures below 1084 °C (melting point of Cu) in N₂ atmosphere to prevent the melting and oxidation of Cu foils. Appropriate sintering aids in N₂ atmosphere need to be developed for high k dielectric materials to have full densification at low temperatures.

In this preliminary work, several additive combinations based on several low softening glasses and fluoride compounds were investigated to improve dielectric performance of BaTiO₃-based dielectrics for the low temperature sintering. There have been numerous reports concerning the utilization of fluoride additives in improving BaTiO₃-based dielectrics. Most of these reports have been focusing primarily on the effects of fluorides on dielectric or ferroelectric properties of BaTiO₃ sintered at temperatures higher than 1100 °C in air atmosphere [8–12]. There have been no systematic reports dealing with the effects of individual fluoride additive, particularly intended for firing at low temperatures in inert atmosphere.

This article intends to define the role of each fluoride compound including AlF₃, BaF₂, CaF₂, LiF and ZnF₂ on the physical and electrical properties of BaTiO₃ modified with low softening glasses. The comparison of air-firing to N₂ firing in terms of phase transition temperature and

maximum dielectric constant is the critical focus of this study.

2 Experimental

Dielectric samples based on BaTiO₃–fluoride–glass compositions were prepared by the conventional solid state reactions of powder mixtures. A commercial BaTiO₃ (99%, Aldrich) powder was admixed with proper contents of glass and fluoride compounds. Four different Pb-free low softening glasses were separately designed and produced by the typical glass melting/quenching process. These four glasses are based on barium titanium borate BaO–Nd₂O₃–TiO₂–B₂O₃ (designated as glass-1), bismuth borosilicate Bi₂O₃–SiO₂–B₂O₃ (glass-2) and two germanate glasses, K₂O–SiO₂–GeO₂ (glass-3) and Bi₂O₃–GeO₂ (glass-4). The unconventional glasses were selected primarily to reduce sintering temperature with the purpose of minimizing undesirable reactions with BaTiO₃ during sintering. Most of silicate or borosilicate-based glasses are known to react chemically with BaTiO₃, which leads to degradation of dielectric constant of BaTiO₃. The BaO–Nd₂O₃–TiO₂–B₂O₃ glass (glass-1) was prepared by melting of the corresponding raw materials mixture at 1450 °C after a soaking time of 1 h and then quenched into a water bath. Glass frit was prepared through the ball-milling process using zirconia ball media for ~12 h. The same process was conducted for glass-2, glass-3 and glass-4 in the different melting conditions of 1100°C for 4 h, 950°C for 1 h and 1050°C for 1 h, respectively [13]. Several fluoride compounds of AlF₃ (99%, High Purity Chemicals), BaF₂ (99%, Acros), CaF₂ (98%, Junsei), LiF (99%, Aldrich), ZnF₂ (99%, Aldrich) were used for this study. Fluoride compounds are known to reduce sintering temperature and to manipulate Curie temperature, depending on the type and content of fluoride [14, 15].

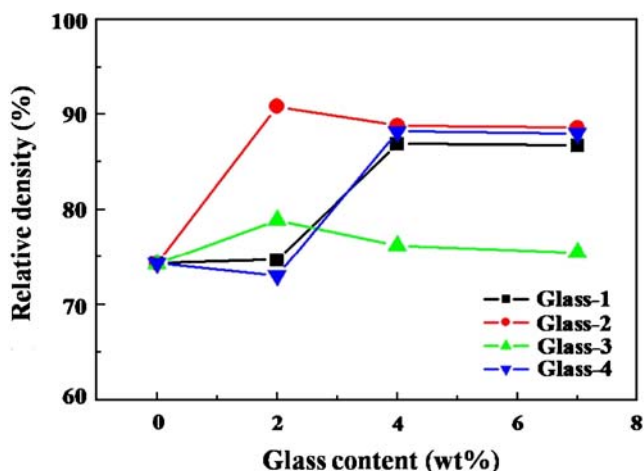


Fig. 1 Density variations of the (97-*x*)BaTiO₃-1.5LiF-1.5ZnF₂-*x*glass samples sintered at 950 °C for 30 min in N₂ atmosphere

Table 1 Softening temperature of each glass and dielectric properties of the (97-*x*)BaTiO₃-1.5LiF-1.5ZnF₂-*x*glass samples fired at 950 °C for 30 min in N₂ atmosphere.

Glass ID	<i>T_s</i> (°C)	Glass content <i>x</i>	Bulk density (g/cm ³)	Dielectric constant (at 1 MHz)	Dielectric loss (at 1 MHz)
Glass-1	650	2	4.50	502	0.010
		4	5.16	483	0.014
		7	5.10	485	0.150
Glass-2	580	2	5.52	1,722	0.020
		4	5.34	1,285	0.042
		7	5.28	980	0.051
Glass-3	560	2	4.68	1,510	0.600
		4	4.5	1,004	0.420
		7	4.44	688	0.480
Glass-4	490	2	4.32	584	0.160
		4	5.28	577	0.085
		7	5.22	812	0.120

T_s Softening temperature

For the effects of different glasses on densification and dielectric properties, the (97-*x*)BaTiO₃-1.5LiF-1.5ZnF₂-*x*glass (*x*=2, 4 and 7) compositions in weight percent were used. Each glass and fluoride additives of LiF and ZnF₂ were admixed by ball milling for 24 h. The powder mixture was completely dried, sieved and pressed at 300 MPa after mixing with a 1.5 wt.% polyvinyl acetate binder. The pressed samples were sintered at 950 °C for 30 min in either air or N₂. For the effects of each fluoride addition, a fixed composition of 95BaTiO₃-2fluoride-3(glass-2) in weight percent was used. Note that only the glass-2 was used for the study of different fluorides. All other procedure to make and sinter pellets was identical.

Bulk density was measured by using the Archimedes principle. The phases of samples sintered in air and N₂ atmosphere were identified by an X-ray diffractometer

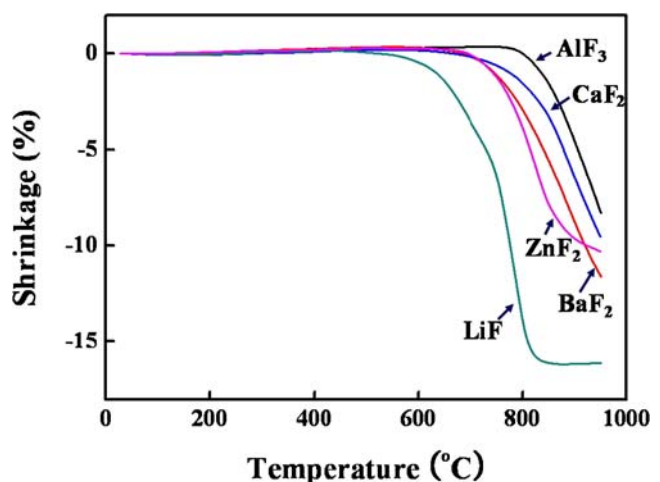
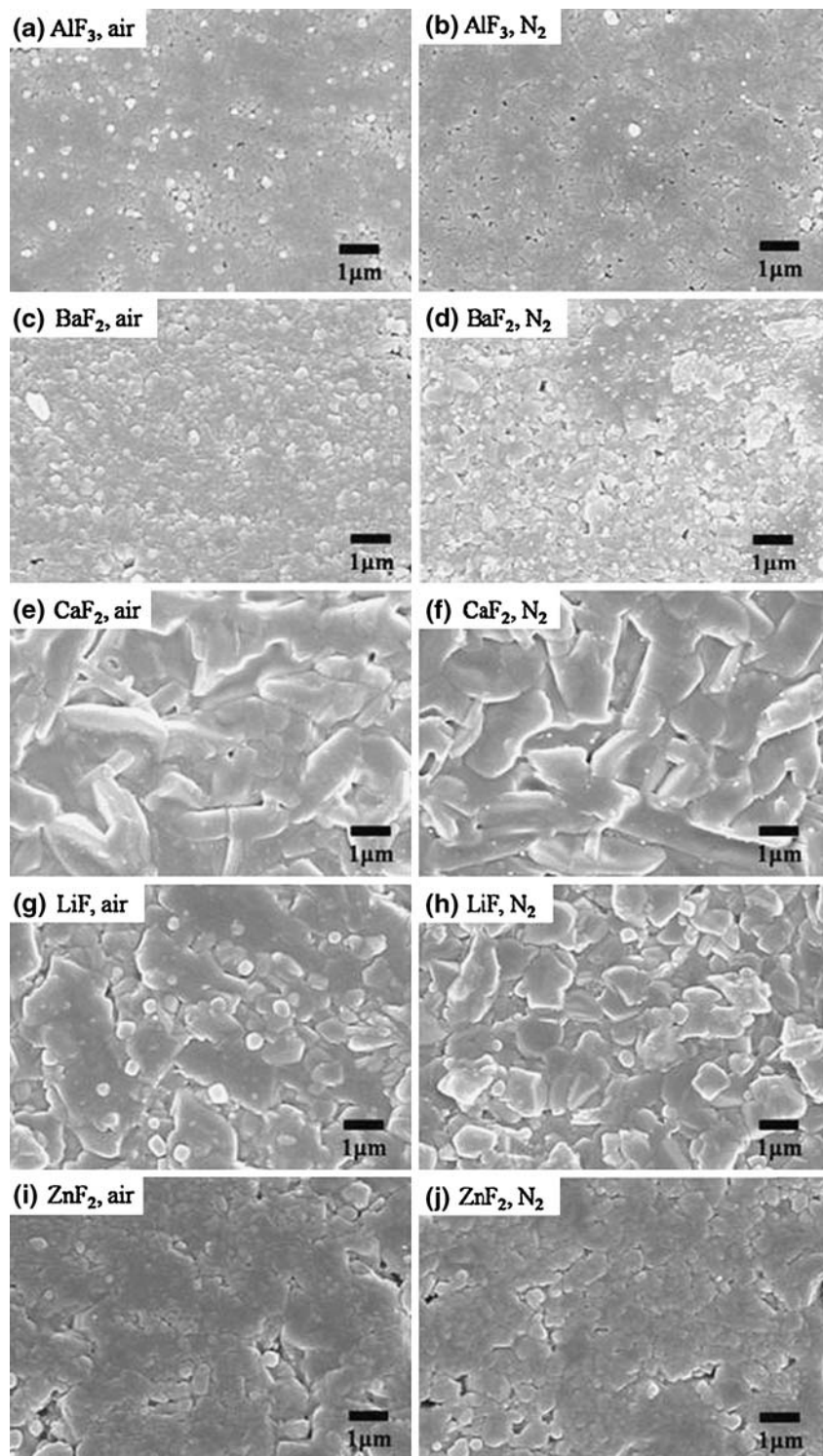


Fig. 2 Shrinkage behavior of the 95BaTiO₃-2fluoride-3(glass-2) samples, measured at a heating rate of 5 °C/min by a dilatometer

Fig. 3 SEM microstructures for the 95BaTiO_3 -2fluoride-3 (glass-2) samples containing (a, b) AlF_3 (c, d) BaF_2 (e, f) CaF_2 (g, h) LiF and (i, j) ZnF_2 , sintered at 950°C for 30 min in air or N_2 atmosphere



(X'pert PRO, PANalytical). The densification behavior were measured by a dilatometer (TD 5000S, MAC science). The microstructures were analyzed using a scanning electron microscope (S-4700, Hitachi). Dielectric properties were measured at 1 MHz using an LCR meter (PM6306, Fluke) coupled in a temperature-controllable chamber.

3 Results and discussion

3.1 Effects of Pb-free glasses

Figure 1 shows the variations in the bulk density of $(97-x)\text{BaTiO}_3$ - 1.5LiF - 1.5ZnF_2 - x glass as a function of

Table 2 Density and dielectric properties of BaTiO₃-based dielectrics with a composition of 95BaTiO₃-2fluoride-3(glass-2), fired at 950 °C for 30 min in air or N₂ atmosphere.

Fluoride additive	Sintering atmosphere	Bulk density (g/cm ³)	Curie temperature (°C)	Dielectric constant (at 1 MHz)		Dielectric loss (at 1 MHz)	
				At RT	At <i>T_c</i>	At RT	At <i>T_c</i>
AlF ₃	Air	3.82	117	549	693	0.027	0.010
	N ₂	3.97	114	317	358	0.024	0.011
BaF ₂	Air	5.23	113	1,245	1633	0.036	0.014
	N ₂	4.65	84	967	1069	0.041	0.016
CaF ₂	Air	4.88	111	908	1134	0.065	0.013
	N ₂	4.43	86	725	798	0.033	0.014
LiF	Air	5.47	15	1388	1425	0.018	0.022
	N ₂	5.48	32	1340	1365	0.022	0.021
ZnF ₂	Air	4.55	-16	1641	2249	0.012	0.056
	N ₂	4.14	-19	1238	1724	0.013	0.037

RT Room temperature, *T_c* Curie temperature

each glass content after firing at 950 °C for 30 min in N₂ atmosphere. It represents that the densification of BaTiO₃ depends not only on the amount of glass but also on the type of glass. It is apparent that BaTiO₃ sintered with glass-2 (Bi silicate) showed most desirable densification performance compared to the other glasses. In the case of glass-2, specifically, the density value of BaTiO₃ was the maximum of ~91% at the glass addition of 2 wt.%. A further increase in glass content does not improve the densification.

Table 1 shows the softening temperature of each glass and dielectric properties of the (97-*x*)BaTiO₃-1.5LiF-1.5ZnF₂-*x*glass samples fired at 950 °C for 30 min in N₂ atmosphere. All glasses possessed pretty low softening points below 650 °C, which must be appropriate for the low temperature densification. The softening points were measured by the differential thermal analysis curves of the glasses. The different density values (Fig. 1) obtained from the individual glass are not possible to have a direct correlation with the softening point since all glasses have low softening points. The density variations with the type and content of glass are likely to be related with certain chemical reactions and diffusion during firing.

Dielectric properties were also influenced by the type and content of glass as shown in Table 1. The overall high dielectric constants were obtained for the glass-2 and glass-3 depending on the content of glass. Particularly, glass-2 showed the highest dielectric constant of 1,722 at 2 wt.% with a low loss of 0.020 at 1 MHz. The case of glass-3 did not show low loss characteristics over the glass contents. The glass-1 and glass-4 samples produced low dielectric constants below 812 regardless of the content of glass. It is suggested that the bismuth silicate glass (glass-2) is promising to keep dielectric constant high after firing. Germanate glasses (glass-3 and glass-4) were not much effective in having both high dielectric constant and low loss tangent, but it depended on the composition of germanate glass as the different results between glass-3

and glass-4 were observed. Although glass-3 had high *k* above >1,000 for the samples with <4 wt.% glass, it was not acceptable from the high dielectric loss that may be partially coming from low fired densities in Fig. 1.

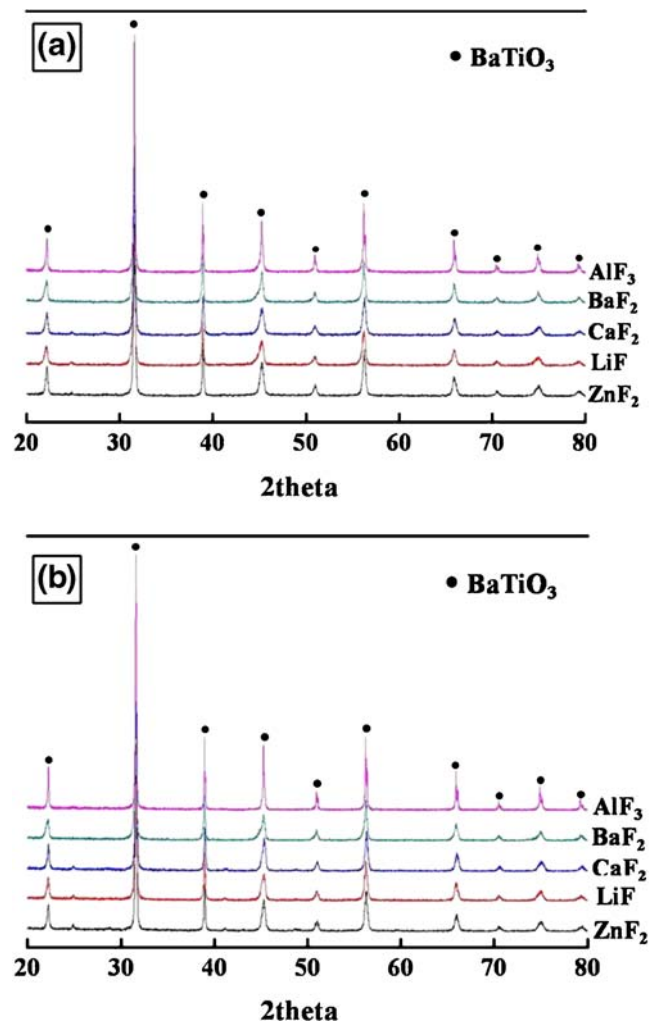


Fig. 4 XRD patterns of the 95BaTiO₃-2fluoride-3(glass-2) samples sintered in (a) air and (b) N₂ atmosphere

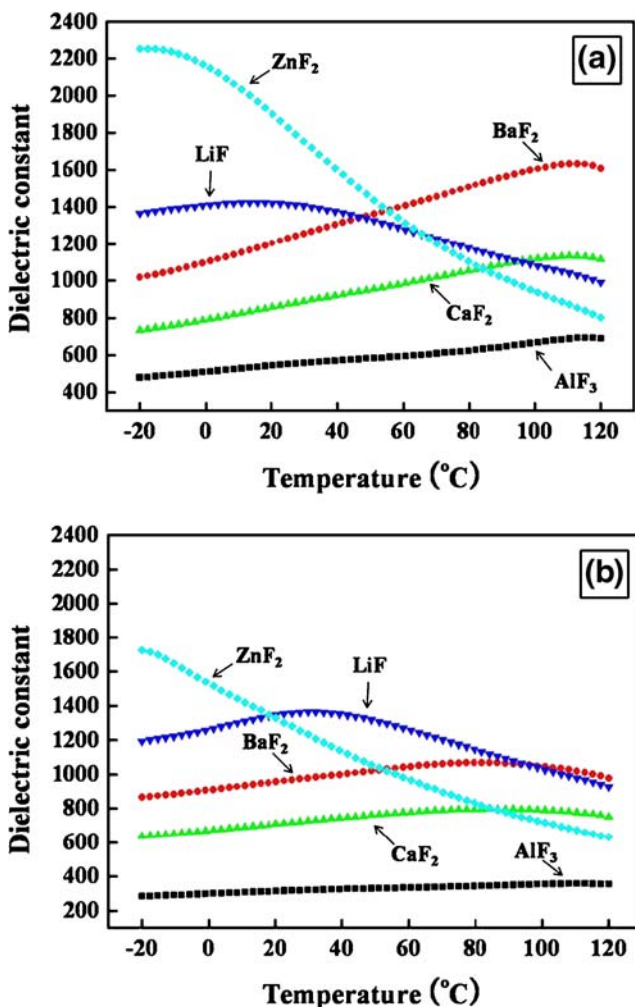


Fig. 5 Temperature dependence of dielectric constant (*k*) for composition of the 95BaTiO₃-2fluoride-3(glass-2) samples sintered in (a) air and (b) N₂ atmosphere

3.2 Effects of fluoride additives

The shrinkage behavior of 95BaTiO₃-2fluoride-3(glass-2) samples containing each fluoride additive such as AlF₃, BaF₂, CaF₂, LiF or ZnF₂ and a fixed 3 wt.% of glass-2 was investigated as shown in the dilatometer curves of Fig. 2. The shrinkage behavior, such as the onset of densification, densification rate and densification temperature range, depended strongly on the type of fluoride additive. Densification of LiF was prominent as it started very early from around 500 °C and ended at ~800 °C. The addition of AlF₃ showed the late densification starting from ~ 820 °C. This observation suggests the interesting fact that the small content of given fluoride is very critical in controlling densification behavior as the maximum ~300 °C difference in the onset densification was found depending on the type of fluoride. When considered the melting point of each fluoride, e.g., LiF ~848 °C, ZnF₂ ~872 °C and AlF₃

~1290 °C [16], the promoted or retarded densification by the selection of fluorides can be understood although some interactions with glass and BaTiO₃ must be involved in a way to affect the densification [17–19]. From the effectiveness of LiF and ZnF₂ in reducing sintering temperature, it is believed that the further reduction in sintering temperature must be possible with low contents of the additives although this work is focusing on the 950 °C application.

Figure 3 shows the microstructures of all samples with each fluoride fired at 950 °C for 30 min in air or N₂ atmosphere. Table 2 summaries bulk density values of the samples. As expected, the addition of AlF₃ resulted in a low density value of regardless of sintering atmosphere and led to smaller grain sizes as shown in Fig. 3(a,b). The LiF case in both air and N₂ firings showed the highest density values ~5.48 g/cm³ as matched well with the trend of shrinkage behavior, presumably coming from the early densification.

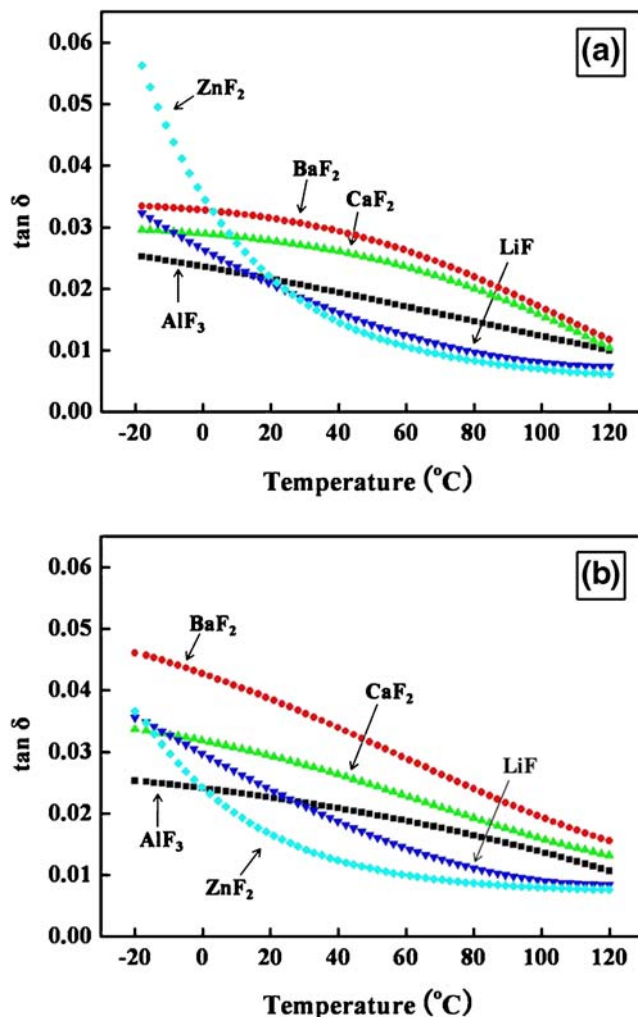


Fig. 6 Temperature dependence of loss tangent (*tanδ*) for composition of the 95BaTiO₃-2fluoride-3(glass-2) samples sintered in (a) air and (b) N₂ atmosphere

The additions of BaF₂, CaF₂ and ZnF₂ which have the densification performance between those of LiF and AlF₃, can be characterized by significant difference in densities between air and N₂ firings. It is noticeable that a high density of ~ 5.23 g/cm³ can be achieved in the case of air-fired BaF₂ sample. Resultant grain size also depended on the type of fluoride but not significantly on the sintering atmosphere (Fig. 3). Distinct larger grain sizes were clearly found in the cases of CaF₂ and LiF samples.

Figure 4 shows the XRD patterns of the 95BaTiO₃–2fluoride–3(glass-2) samples fired at 950 °C for 30 min in air and N₂ atmosphere. There was no distinct difference in the patterns between air and N₂-firings for all fluoride additives. Phase-pure BaTiO₃ peaks were observed in all samples although some unknown peak traces, e.g., at ~25° of 2θ, were seen in the cases of CaF₂, LiF and ZnF₂.

Figures 5 and 6 demonstrate the temperature dependence of dielectric constant and dielectric loss over the temperature range of –20 to 120 °C, which were measured at 1 MHz for the 95BaTiO₃–2fluoride–3(glass-2) samples fired at 950 °C for 30 min in air and N₂ atmosphere. Table 2 represents some important values, including T_c (transition temperature), k at room temperature (RT), k at T_c, tanδ at RT and tanδ at T_c, based on the figures. Basically, T_c, k and tanδ were dependent predominantly on the choice of fluoride although it is very difficult to be understood by the existence of phase or the degree of densification. The overall dielectric constants were much lower in N₂-firing than in air-firing. The dielectric result brought by ZnF₂ looked most promising particularly at room temperature. The highest dielectric constant of 1,641 in air (k~1,238 even in N₂) with a reasonably low loss of 0.012 as the RT values can be considered crucial for developing decoupling capacitors for Cu-PCB applications. The cases of BaF₂ and LiF were also thought to be acceptable from their dielectric performance. Particularly, the addition of LiF resulted in a T_c value close to room temperature and showed minimal difference in k between the air and N₂ firings while keeping dielectric loss low. The AlF₃ samples showed least performance with lowest k over the temperature range regardless of firing atmosphere.

In regard to dielectric requirements, it is important for capacitors to represent minimal fluctuation in dielectric constant over the temperature range while raising dielectric constant as high as possible. For decoupling capacitors, X7R-type dielectric materials having no more than ±15% from its reference value at 25 °C between –55 and 125 °C are usually preferred. Accordingly, the ZnF₂ sample exhibiting the highest dielectric constant may not be applicable due to the high fluctuations of dielectric constant with temperature.

It is very interesting to observe that T_c varied significantly depending on the choice of fluoride additive. The

Curie temperatures of LiF and ZnF₂ were around room temperature or below, while AlF₃, BaF₂ and CaF₂ exhibited high ones of around 115 °C. It is known that the Curie transition temperature in ferroelectric materials can be influenced by many factors including chemical modification, particle size and crystal imperfections [20, 21].

4 Conclusions

This preliminary work on compositional studies for nitrogen-fireable embedded capacitors concluded that dielectrics based on BaTiO₃ with bismuth borosilicate glass and fluoride additives such as AlF₃, BaF₂, CaF₂, LiF and ZnF₂ had a great potential in terms of physical and dielectric performance. The bismuth borosilicate was selected as the most promising one in terms of densification and dielectric constant compared to other non-Pb low temperature glasses. The densification and dielectric performance were largely affected by the choice of fluoride. As a promising example, the 95BaTiO₃–2LiF–3(Bi borosilicate) sample showed k~1,340 and tanδ~0.022 at room temperature when fired at 950 °C in N₂.

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