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Correlation of Wettability and Interfacial Reaction to the Densification and Dielectric Properties of Fluxed-BaTiO₃

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Abstract-Reducing the sintering temperature of BaTiO₃ has typically been achieved through the use of a fluxing agent to promote densification by liquid phase sintering. Liquid phase formation in these systems is due either to the melting of the flux or to the formation of a eutectic liquid between the flux and BaTiO₃. In this paper, the correlation between the wettability and interfacial reactions between fluxes and BaTiO₃ with respect to the densification behavior associated with liquid phase sintering, and the resulting dielectric properties is presented. Fluxes used in this study include 5ZnO·2B₂O₃, 5CdO·2SiO₂, Pb₅Ge₃O₁₁, CuO·TiO₂, 3Bi₂O₃·B₂O₃, and LiF.

INTRODUCTION

The wettability of fluxes on a ceramic is very important for densification during sintering. A non-wetting liquid, $\theta > 90^\circ$, may lead to swelling of the compact during sintering, segregation, and possible melt extrusion through open porosity. A wetting liquid, $\theta < 90^\circ$, will attempt to occupy the lowest free energy positions and hence will preferentially flow into fine scale porosity due to capillary forces.^{1,2} When there is insufficient liquid to fill all of the porosity, these capillary forces will pull the particles together to minimize the free energy. This effect gives rise to the rearrangement stage and rapid initial densification during liquid phase sintering. Usually wetting is aided by solubility of the solid in the liquid or the formation of intermediate compounds.

In addition to serving as a liquid phase to promote densification, the fluxes may act as a second phase layer to dilute the dielectric properties, or serve as a Curie point shifter for BaTiO₃ when they are incorporated into the BaTiO₃ lattice. The characteristics of grain boundary phases in ceramics, such as composition, connectivity, volume fraction, and defect chemistry, can have a significant impact on their dielectric properties. If the liquid phase has a low solubility in BaTiO₃ and is persistent throughout liquid phase sintering, then the solidified, interconnected liquid phase surrounding the BaTiO₃ will result in an intergranular boundary layer. The dielectric properties will be diluted, and can be modeled by the brick wall model. On the other hand, if the liquid phase has a high solubility in BaTiO₃ and acts as a transient phase during liquid phase sintering, then the dilution of the dielectric properties is reduced.³

In this study, the correlation between the wettability and interfacial reactions with respect to the densification behavior associated with liquid phase sintering, and the resulting dielectric properties is characterized. Although the formation of low melting temperature fluxes described in the literature have been complex, several simple flux systems, including 5ZnO·2B₂O₃, 5CdO·2SiO₂, Pb₅Ge₃O₁₁, CuO·TiO₂, 3Bi₂O₃·B₂O₃, and LiF, which have been shown to be effective sintering additives,³⁻⁸ were selected for use in this work.

EXPERIMENTAL PROCEDURE

Commercial TAM-HPB BaTiO₃ and Pb₅Ge₃O₁₁, 3Bi₂O₃·B₂O₃, 5CdO·2SiO₂, CuO·TiO₂, 5ZnO·2B₂O₃, and LiF fluxes were used in this study. Except for the LiF and CuO·TiO₂ systems, the raw materials for each flux were mixed/milled in methyl alcohol in a polyethylene jar with ZrO₂ media using a ball mill. After drying, these powders were transferred to a platinum crucible and heated at a temperature elucidated from DTA/TGA analyses. Following melting, they were quenched and then milled to pass through a 320 mesh screen. For the microstructural development and dielectric properties studies, these fluxes were also mixed/milled with the BaTiO₃ to achieve submicron particles. For the contact angle determinations, the fluxes were pressed into 0.254 cm (0.1-in) diameter pellets.

Wetting experiments were carried out in a tube furnace in air

using the Sessile-drop method. Contact angles were double-checked through optical observations of cross-sections. Temperatures of liquid phase formation at each flux system were also determined using DTA with a heating rate of 10°C/min on BaTiO₃ powders mixed with excess flux (20wt%). Pellets of mixtures also were heated up to 1100°C and quenched, followed by XRD analysis on the polished surface to obtain the phases that were solidified or decomposed from the liquid phase during cooling.

HPB BaTiO₃ was mixed/milled for 24 h with specific volume fractions of fluxes in methyl alcohol using a Sweco mill (polyethylene jar, ZrO₂ media). Dried powders were characterized (particle size $\approx 0.7 \mu\text{m}$) and mixed with DuPont 5200 binder and then pelletized. Pellets were sintered at 900-1150°C for 2 h (heating rate: 6°C/min, cooling rate: 3°C/min).

Dilatometric analyses were performed to characterize the shrinkage of the flux-sintered BaTiO₃ with temperature at a heating rate of 3°C/min. The dilatometric curves were compared with the temperature of liquid formation, which was obtained using DTA, although the heating rates of the DTA and dilatometric analyses were slightly different.

RESULTS AND DISCUSSION

1. Wettability and Reaction of Fluxes on BaTiO₃

Results of Sessile drop experiments for various fluxes on BaTiO₃ substrates are given in Table 1. Four types of Sessile drop configurations were observed in this study. The first type has no compositional changes in the flux, and only trace amount of fluxes

Table 1 Wetting Angles of Various oxides on the BaTiO₃ substrate

Compounds	Temperature (°C)	Contact Angle (°)
LiF	875	0
BaLiF ₃	850	12
PbO	900	0
Pb ₅ Ge ₃ O ₁₁	750	8
Bi ₂ O ₃	800	0
B ₂ O ₃	460	73
	600	36
	800	11
3Bi ₂ O ₃ ·B ₂ O ₃	750	19
5CdO·2SiO ₂	1200	14
5ZnO·2B ₂ O ₃	1050	(before rxn) 32
		(after rxn) 24
CuO·TiO ₂	1050	(before rxn) 61
		(after rxn) 22

diffuse into BaTiO₃; 3Bi₂O₃·B₂O₃ is an example from this study. The second type exhibits a chemical reaction between the BaTiO₃ and flux, which results in spreading ($\theta = 0$); LiF and Bi₂O₃ are examples from this study. The third type exhibits complete solubility of the flux in the BaTiO₃, which results in spreading; PbO is an example from this study. The fourth type has an acute contact angle owing to a high solubility of BaTiO₃ in the flux, and a limited solubility of the flux in the BaTiO₃; BaLiF₃, Pb₅Ge₃O₁₁, 5CdO·2SiO₂, CuO·TiO₂, and 5ZnO·2B₂O₃ are examples from this study.

The melting temperatures of flux components and those of possible eutectic liquids between fluxes and BaTiO₃ were measured by DTA on mixtures of BaTiO₃ and 20 wt% fluxes with a heating rate of 10°C/min. The results are summarized in Table 2. Details of these results are discussed below:

(i) LiF System

LiF has been shown to be an effective sintering aid for BaTiO₃ by several investigators.⁴ During sessile drop measurements, rapid spreading ($\theta = 0^\circ$) was observed at the melting temperature of LiF. XRD analyses on the surface of the LiF-wetted specimen of BaTiO₃ indicated that BaLiF₃ and LiTiO₂ formed. Formation of these compounds was also reported by Lin, while Bonnet et al. and Anderson et al. showed the presence of Li₂TiO₃ in their study.

As shown by the DTA results (Table 2), a eutectic melt is formed at 750°C from mixtures of BaTiO₃ and LiF. Comparing this result with the phase diagram of BaLiF₃-LiF, it seems that the melt that forms at 750°C is due to the eutectic reaction between BaLiF₃ and excess LiF. During cooling, the eutectic liquid recrystallized into LiTiO₂ and BaLiF₃. Results from DTA studies on mixtures of BaTiO₃ and LiF with addition of BaCO₃ show endothermic peaks at 632 and 720°C, which correspond to eutectic liquid formation. This correlates well with studies that have shown LiF additions to Ba-excess BaTiO₃ (adjusted by BaCO₃) lower the sintering temperature.

BaLiF₃, an intermediate product in the LiF-wetted specimen of BaTiO₃, has also been shown to be an effective sintering aid. The wetting angle was found to be 12°. DTA results show that mixtures of BaTiO₃ and BaLiF₃ did not exhibit any liquid formation other than the incongruent melting of BaLiF₃ at 845°C.

(ii) Bi₂O₃-B₂O₃ System

DTA results on a mixture of BaTiO₃ and Bi₂O₃ showed the presence of three endothermic peaks at 575, 719, and 789°C, and the α -Bi₂O₃ to δ -Bi₂O₃ at 728°C. These three peaks are most likely due to eutectic liquid formation, although further studies would be needed to confirm this hypothesis. The first two endothermic peaks are very small. During the wettability study, no visible reaction was observed at temperatures below the melting point of Bi₂O₃, which is 807°C. Above the melting temperature, a rapid spreading of Bi₂O₃ on BaTiO₃ was obtained. XRD analyses on the surface of Bi₂O₃-wetted

Table 2 DTA results of oxides and mixtures, which shown the endothermic peaks corresponding to the temperature at which liquid formed

Compounds	Melting Point (°C)
LiF	865
BaLiF	845
BaTiO ₃ +LiF	750
BaTiO ₃ +BaLiF ₃	845
BaTiO ₃ +LiF-BaCO ₃	632
	720

PbO	886
GeO	1115
BaTiO ₃ -GeO	1083
Pb ₂ Ge ₃ O ₁₁	742
BaTiO ₃ +Pb ₂ Ge ₃ O ₁₁	736
	781

Bi ₂ O ₃	807
B ₂ O ₃	450
3Bi ₂ O ₃ -B ₂ O ₃	625
BaTiO ₃ -Bi ₂ O ₃	575
	719
	789
BaTiO ₃ +3Bi ₂ O ₃ -B ₂ O ₃	542
	655
	768

SiO	1723
5CdO-2SiO ₂	1191
BaTiO ₃ +5CdO-2SiO ₂	1046

5ZnO-2B ₂ O ₃	1043
BaTiO ₃ +5ZnO-2B ₂ O ₃	834

CuO-TiO ₂	1034
BaTiO ₃ +CuO	1030
BaTiO ₃ -CuO-TiO ₂	1024

specimen of BaTiO₃ show the presence of Bi₂O₃ and a small amount of BaBi₄Ti₄O₁₅.⁵

A glass former, B₂O₃, was added to the Bi₂O₃ (3Bi₂O₃-B₂O₃) to determine its affect on the wettability and sintering behavior. DTA results showed the temperature of the three endothermic peaks associated with liquid phase formation were lowered by the B₂O₃ additions to 542, 655, and 768°C. The wetting angle of 3Bi₂O₃-B₂O₃ was 19° at 750°C. XRD analysis on a mixture of BaTiO₃ and 20wt% 3Bi₂O₃-B₂O₃ cooling from 1100°C show that a glass phase, Bi₂O₃,

and small amounts of BaBi₄Ti₄O₁₅ phases exist. Subbarao et al have suggested that BaBi₄Ti₄O₁₅ forms at \approx 800°C, and redissolves at higher temperatures.

(iii) 5PbO-3GeO₂ System

Wetting studies showed that PbO readily spread on BaTiO₃ at temperatures greater than its melting temperature of 886°C. Pb₅Ge₃O₁₁ was first reported by Payne as a flux for BaTiO₃, providing a high dielectric constant and breakdown strength and a low dissipation factor.⁶ As shown by the DTA results, Pb₅Ge₃O₁₁ is another flux that exhibits a eutectic melting point lower than 800°C. The two temperatures associated with liquid phase formation are the melting of Pb₅Ge₃O₁₁ at 736°C and a eutectic liquid between Pb₅Ge₃O₁₁ and BaTiO₃ at 781°C. The wetting angle of this flux on BaTiO₃ is 8°.

(iv) 5CdO-2SiO₂ System

Cadmium silicates, such as 2CdO-SiO₂, 5CdO-2SiO₂, and 3CdO-SiO₂ have been used as fluxes for BaTiO₃, as first reported by Maher. Among these compounds, 5CdO-2SiO₂ was found to be the most effective sintering aid. 5CdO-SiO₂ has a melting temperature at 1191°C (Table 2). Mixtures of 5CdO-SiO₂ and BaTiO₃ exhibit a eutectic temperature at 1046°C. The wetting angle of 5CdO-SiO₂ on BaTiO₃ was found to be 14° at 1200°C. XRD analysis on a mixture of BaTiO₃ and 20wt% 5CdO-2SiO₂ quenched from 1100°C shows the existence of CdO and BaCdSi₂O₇. The formation of BaCdSi₂O₇ may explain the precipitation of CdO, which was observed in Maher's study.⁷

(v) 5ZnO-2B₂O₃ System

Similar to the CdO-2SiO₂ system, mixtures of 5ZnO-2B₂O₃ and BaTiO₃ exhibited eutectic liquid phase formation at 834°C, which is much lower than the melting point of the flux itself (1043°C). The wetting angle before visible reaction occurs is 32°, and after reaction is 24°. XRD analysis on a mixture of BaTiO₃ and 5wt% 5ZnO-2B₂O₃ heated to 1100°C revealed the presence of ZnO and an unknown phase.

(vi) CuO-TiO₂ System

The addition of CuO to BaTiO₃ results in eutectic liquid formation when CuO partially decomposes at 1070°C according to the reaction: 4 CuO \leftrightarrow 2 Cu₂O + O₂ (equilibrium PO₂ \approx 0.4x10⁵ Pa at 1070°C¹³⁵). With the addition of TiO₂, the eutectic temperature is reduced to 1024°C (Table 2). Hennings showed that on cooling, a Cu₃TiO₄ phase recrystallized, although the results from this study could not confirm the identification of the recrystallized phase.⁸ There exist over 20 compounds in the CuO-TiO₂ system. The wetting angle of CuO-Cu₂O-TiO₂ on BaTiO₃ is initially 61° at 1050°C, which is very high for liquid phase sintering. However, with time the CuO-Cu₂O-TiO₂ eutectic liquid reacts with the BaTiO₃ and reduces the contact angle to 22°. There must be a limited solubility of BaTiO₃ in the flux, since Hagemann's studies showed that excessive additions of CuO-TiO₂ reduced the densification.

2. Relationship of the Wettability and Solubility to the Densification Behavior of Fluxed-BaTiO₃

The temperature at which liquid phase formation occurs directly impacts dimensional changes during densification of a ceramic. This is especially significant for some flux systems that exhibit more than one liquid phase formation temperature. Liquid formation may affect the densification process through changing the volume of the liquid phase, the wettability of the liquid, the solubility of the solid in the melt, and the formation of recrystallized solid compounds.

Figure 1 shows the dilatometric results and corresponding DTA curves, which exhibit two types of sintering behavior. The first type contains one sintering step that occurs at the temperature of liquid phase formation. In this case this corresponded to the 5.0 wt% (4.0 v%) 5CdO-2SiO₂ (Figure 1a) and 5.0 wt% (7.0v%) 5ZnO-2B₂O₃ (Figure 1b) fluxes. Sintering proceeded with increasing temperature

until the samples were densified. The second type of sintering behavior exhibits more than one shrinkage step, such as for the 10 wt% (8.1v%) $3\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ and 2 wt% (4.5 v%) LiF (Ba/Ti=1.02), as shown in Figures 1c and 1d. The changes in shrinkage rate correspond to the temperatures at which different liquid phases form associated with solid particle formation. In the case of BaTiO_3 with $3\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$, the contraction below 650°C is negligible, even though there is a small endothermic peak at 542°C , as indicated in the DTA curve. This is due to a trace amount of liquid phase generation. Eutectic liquid phase formation at the interface between solid BaTiO_3 and solid $3\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ at temperatures $<700^\circ\text{C}$ was kinetically limited. The change in shrinkage rate at $\approx 800^\circ\text{C}$ corresponds to the melting point of Bi_2O_3 . $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ was observed after quenching, but it is unknown whether it is present at high temperatures, as suggested by Subbaro.

For the BaTiO_3 with LiF additions (Ba/Ti=1.02, adjusted by BaCO_3), the onset of densification at $\approx 600^\circ\text{C}$ corresponds to the

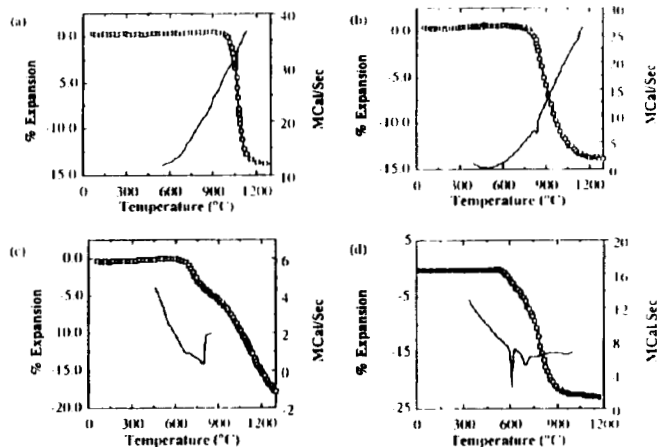


Figure 1. Dilatometric results and DTA curves of BaTiO_3 with (a) 5wt% of $5\text{CdO}\cdot 2\text{SiO}_2$, (b) 5wt% $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$, (c) 10wt% of $3\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$, and (d) 2wt% LiF (2wt% BaCO_3 addition).

inflection point at 123°C , suggesting that a grain core-shell structure is formed.

For the $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$, $5\text{CdO}\cdot 2\text{SiO}_2$, $\text{CuO}\cdot\text{TiO}_2$, and $3\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ systems, there was no apparent grain growth and no shift in the Curie point. However, the magnitudes of the dielectric constant are tremendously different. The dielectric constant of BaTiO_3 with 10wt% of $3\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ is only 1300 at room temperature, and that of BaTiO_3 with 5wt% of $5\text{CdO}\cdot 2\text{SiO}_2$ is 3400. The density, volume, and connectivity of the flux are the factors that contribute to

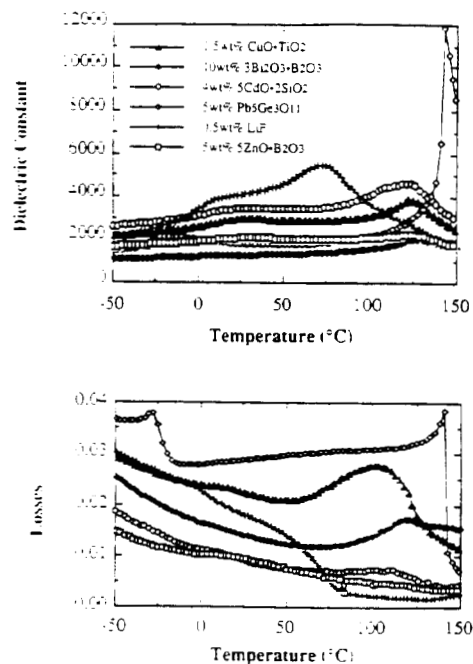


Figure 2. Dielectric constant and losses of BaTiO_3 sintered with various fluxes at 1000°C for 2 hours.

Table 3 Characteristics of dielectric properties of BaTiO_3 sintered with various oxides

Flux Composition	Wt% Added	Density (g/cm ³)	Grain Size (μm)	K_{100}	K_{10}	$(\text{Tan}\delta)_{10}$	T_c ($^\circ\text{C}$)
$5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$	5	5.71	0.7	2300	2100	0.01	124
$\text{Pb}_5\text{Ge}_3\text{O}_{11}$	5	5.99	6	12000	1800	0.03	144
$0.74\text{Bi}_2\text{O}_3\cdot 0.26\text{B}_2\text{O}_3$	10	5.64	0.7	2100	1300	0.01	126
LiF (Ba/Ti=1.02)	0.5	5.89	1.5	5500	4100	0.02	70
$5\text{CdO}\cdot 2\text{SiO}_2$	4	5.91	0.7	4600	3400	0.01	122
$\text{CuO}\cdot\text{TiO}_2$	1.5	5.54	0.7	3900	3000	0.02	123

eutectic liquid between LiF· BaCO_3 . The change in shrinkage at $\approx 720^\circ\text{C}$ is due to the formation of another eutectic liquid formation.

3. Dielectric Properties

The dielectric constant and losses of BaTiO_3 sintered with various fluxes measured at 1000 Hz are shown in Figure 2 and summarized in Table 3. The losses of these systems are all less than 3%. For BaTiO_3 sintered with $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and LiF, the Curie points were shifted, while $5\text{CdO}\cdot 2\text{SiO}_2$ additions broadened the transition. BaTiO_3 -5wt% $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ exhibits a sharp transition at 143°C , and confirms the formation of a Ba(Pb)TiO₃ solid solution. BaTiO_3 -0.5wt% LiF exhibits a diffuse phase transition located at 73°C with an

these changes in the dielectric constant. Comparing the dielectric constant with the amount of flux added one concludes that residual grain boundary phases must be strongly affecting the dielectric constant.

SUMMARY

Eutectic melts form during sintering of fluxed- BaTiO_3 . Observed wetting angles of the fluxes on BaTiO_3 were distributed between 65° and 0° (spreading). The wettability of a flux on BaTiO_3 substrate was enhanced if a eutectic reaction or significant interdiffusion occurred. The appearance of the liquid phase correlated directly with a sharp change in the sintering rate. The wettability and

intersolubility of flux on BaTiO₃ significantly altered the dielectric properties due to porosity formation and the characteristics of the grain boundary. Lower contact angles and interdiffusion of fluxes resulted in lower residual porosity and lower volume fractions of an interconnected second phase.

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