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Effects of Calcination Temperature and A/B Ratio on the Dielectric Properties of (Ba,Ca)(Ti,Zr,Mn)O_3 for Multilayer Ceramic Capacitors with Nickel Electrodes

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The electrical performance of multilayer ceramic capacitors (MLCCs) with Ni inner electrodes, made from (Ba,Ca)-(Ti,Zr,Mn)O_3 (BCTZM), is closely related to the calcination temperature and the A/B ratio of the powder. For materials showing A/B = 1.000, the lifetime, the breakdown voltage, and the RC increase with higher calcination temperatures. No significant effect of the calcination temperature on RC and lifetime was found for materials showing A/B = 0.991. The isoelectric point of BCTZM is shifted toward higher pH values when the calcination temperature is decreased. The above results are attributed to the colloidal stability of aqueous BCTZM suspensions and the resulting green density of powder compacts.

I. Introduction

(Ba,Ca)(Ti,Zr,Mn)O_3 (BCTZM) is commonly used as a basic material for multilayer ceramic capacitors (MLCCs) with the temperature specification Y5V. Ca and Zr are employed for broadening and shifting the dielectric maximum at the Curie point (T_C) to room temperature. Mn is used as a strong acceptor for trapping conduction electrons, when MLCCs are cofired with Ni base metal electrodes (BMEs) in reducing atmosphere. A previous report by Sumita *et al.*[1] stresses the influence of the calcination temperature of BCTZM on the lifetime stability. They claimed that calcination at higher temperatures significantly improves the lifetime of MLCCs.

The fundamental reason for the calcination effect on the lifetime is not yet fully understood. The present work deals with the influence of small changes of the A/B ratio and the calcination temperature on the microstructure and lifetime stability of MLCCs prepared from BCTZM.

II. Experimental Procedure

The experimental material BCTZM with the standard composition $(Ba_{0.86}Ca_{0.14})(Ti_{0.85}Zr_{0.14}Mn_{0.01})O_3$ was prepared from reagent-grade $BaCO_3$, $CaCO_3$, TiO_2, ZrO_2, and $MnCO_3$. Mn was incorporated on the B-sites, according to the observed[2] solubility of Mn on B-sites of >1.5 mol%. Materials showing two different atomic ratios of A-site ions (Ba, Ca) and B-site ions (Ti, Zr, Mn) have been prepared: material I, A/B = 1.000 ± 0.0015; material II, A/B = 0.991 ± 0.0015. The A/B ratio was carefully fixed by analytical means (XRF). The raw materials were mixed in aqueous suspension in a ball-mill, using Y-stabilized zirconia balls of 2 mm diameter. The powder mixtures were calcined for 12 h in air at 900°, 1000°, 1100°, and 1200°C in air.

For manufacturing of green MLCC chips a water-based tape casting technique was employed. For slurry preparation the calcined powder was milled to a particle size of d_{50} = 1.0 μm and mixed with PVA binder solution, dispersant, defoamer agent, plasticizer, and water. Dielectric layers were printed with a Ni electrode pattern and stacked under appropriate pressure (210 bar) and heat. Green chips of size "0805" (EIA Code 0.08 in. × 0.05 in.) with 20 dielectric layers of 15 μm (sintered thickness) were formed by cutting. Binder burnout was carried out at 250°C for 10 h. MLCCs were fired at 1300°C for 2 h in a reducing atmosphere of moist nitrogen and hydrogen, having an oxygen partial pressure of $\approx 10^{-14}$ bar. After sintering, the MLCCs were annealed for re-oxidation at 900–1200°C in N_2/O_2 having an oxygen partial pressure of $\approx 10^{-4}$ bar. The copper terminations were dipped and fired at 850°–900°C at an oxygen partial pressure of $\approx 10^{-4}$ bar. The microstructure of sintered samples was examined by scanning electron microscopy (SEM; Hitachi Model S2500). The capacitance and the dissipation factor were measured at 1 kHz/0.5 V_{rms}, using an HP 4194A bridge. The insulation resistance (IR) was determined after applying 50 V for 60 s. The lifetime stability of the dielectric material was ascertained by means of highly accelerated lifetime tests (HALT) at 140°C and 300 V (20 V/μm).

Dispersions for micro-electrophoresis were prepared by mixing about 0.01 g of each BCTZM powder to give a concentration of 10^{-3} mol/L H_2O, using an ultrasonic bath. The pH of the dispersions was adjusted by adding a few drops of either 0.01*M* HCl or NaOH followed by thorough mixing. The zeta potential of the BCTZM powder was measured as a function of pH, using a commercial Lazer Zee Meter. Ammonium polyacrylate with a molecular weight of about 4000 was used to disperse BCTZM ceramic powder in water. Sedimentation of BCTZM slurries was studied as a function of the calcination temperature. Before sedimentation tubes were filled, the slurries were milled in an attritor for 2 h. All tubes were filled at the same level and all slurries contained the same amount of ceramic powder (solid content 60 wt%) and 0.8 wt% ammonium polyacrylate dispersant (DISPEX-A, Allied Colloids, Hamburg, Germany). The sedimentation levels were measured when they did not change any more (i.e., after a few days). The green density was determined from the ratio of weight and volume and the fired density by means of the Archimedes method.

III. Results and Discussion

(1) XRD Studies

X-ray diffraction (XRD) revealed $BaCO_3$ second phase in all BCTZM powders calcined at temperatures <1100°C, independent

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Table I. Effect of Calcination Temperature on the Electrical Properties of BCTZM MLCCs†

	A/B = 1.000				A/B = 0.991			
$T_{calcin.}$ (°C)	K_{max}	T_C (°C)	IR ($\times 10^{10}$ Ω)	HALT (ave h)	K_{max}	T_C (°C)	IR ($\times 10^{10}$ Ω)	HALT (ave h)
900	7850	16	26.2	7.4	8900	45	16.2	6.9
1000	8100	15	28.6	8.6	8500	45	14.8	7.2
1100	8300	12	30.9	10.0	9400	45	14.5	7.4
1200	9100	11	32.4	11.6	10500	45	14.2	7.1

†Twenty dielectric layers of 15 μm; highly accelerated lifetime test (HALT) at $E = 20$ V/μm and 140°C.

of the A/B ratio. The estimated detection limit of $BaCO_3$ was ≈1 mol%. While the $BaCO_3$ peak was almost identical for A/B = 1.000 and A/B = 0.991 after calcination at 900°C, it became weaker at 1000°C for A/B = 0.991. All powders calcined at temperatures >1100°C no longer showed peaks of $BaCO_3$ second phase.

(2) Electrical Properties

Table I shows the measured values of the maximum dielectric constant (K_{max}) at the Curie point (T_C), the insulation resistance (IR), and the average lifetime under HALT stress for A/B = 1.000 and 0.991 and calcination temperatures in the range 900° to 1200°C. K_{max} was found to increase for both A/B ratios with higher calcination temperatures. Significant changes of T_C, IR, and HALT were observed only for A/B = 1.000 with increasing calcination temperature. A remarkable effect was the large scatter of RC and lifetimes observed in HALT of MLCCs showing A/B = 1.000. MLCCs of materials with A/B = 0.991 showed in contrast much smaller scatter of IR and lifetime. This result is in full agreement with that of Sumita,[1] who studied $BaTiO_3$ with Ba excess. However, it is important to note that the lifetime is obviously independent of the calcination temperature for A/B = 0.991, i.e., for A/B < 1.

The influence of the calcination temperature on RC and the breakdown voltage, V_{bd}, is shown in Figs. 1 and 2. For A/B = 1.000, RC and V_{bd} gradually increased with increasing calcination temperature, while for A/B = 0.991 the calcination temperature had only little influence. Once again, the results of RC and V_{bd} illustrate the different influence of the calcination temperature on materials showing A/B = 1.000 and A/B = 0.991. These results confirm earlier observations[3] that the effect of the calcination temperature on the electrical properties is different even for small changes of the A/B ratio.

(3) Microstructure Examination

Figures 3 and 4 show the influence of the calcination temperature on the microstructure of MLCCs prepared from materials showing different A/B ratios of 1.000 and 0.991. Samples with A/B = 1.000 (Fig. 3) exhibited a smaller grain size than those of materials with A/B = 0.991 (Fig. 4). In contrast to A/B = 1.000, no significant influence of the calcination temperatures on the grain size was observed for A/B = 0.991, although the grains were remarkably larger. Waser[4] reported that $BaTiO_3$-based compositions with A/B < 1 exhibit a stronger trend to degradation than those showing A/B > 1. Since the Ti-rich second-phase $Ba_6Ti_{17}O_{40}$ was found to be stable toward degradation,[5] our results should be interpreted in the light of grain size effects.[6] This interpretation offers a plausible explanation of the influence of the calcination temperature on the lifetime of BCTZM with different A/B ratios. Corresponding to the larger grain size, the lifetime of samples showing A/B = 0.991 should be shorter than that of A/B = 1.000. In the case of A/B = 0.991 no significant influence of the calcination temperature on the grain size as well as on the lifetime of MLCCs was observed. The large scatter of lifetime and IR observed in MLCCs with A/B = 1.000 may be explained in terms of the broader grain size distribution observed in these samples (Fig. 3).

The observation of the microstructure gives a more consistent picture of the influence of the calcination temperature on the electrical properties of MLCCs, showing different A/B ratios of 1.000 and 0.991. However, the different effect of the calcination temperature on the microstructures of both series it is not yet understood.

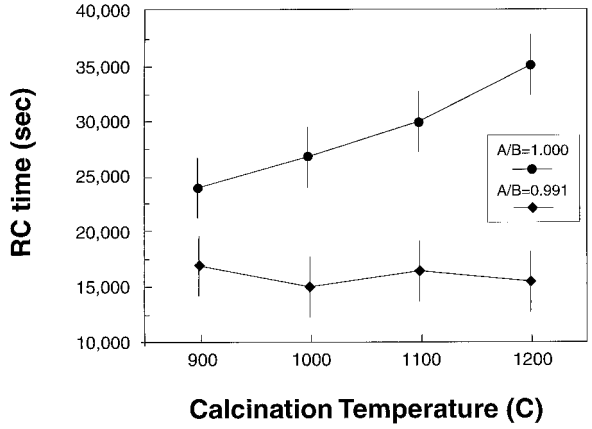

Fig. 1. RC time as a function of calcination temperature for BCTZM with A/B = 1.000 ± 0.0015 and A/B = 0.991 ± 0.0015, sintered at 1300°C in 99/1 N_2/H_2 at $p_{O_2} \approx 10^{-14}$ bar.

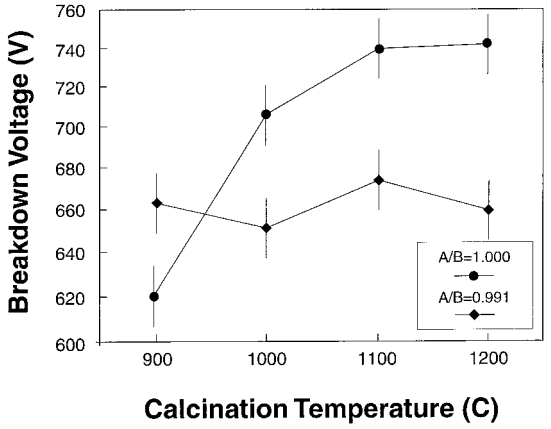

Fig. 2. Breakdown voltage (V_{bd}) as a function of calcination temperature for BCTZM with A/B = 1.000 ± 0.0015 and A/B = 0.991 ± 0.0015, sintered at 1300°C in 99/1 N_2/H_2 at $p_{O_2} \approx 10^{-14}$ bar.

(4) Zeta Potential and Sedimentation Measurement

The electrophoretic mobility of BCTZM powders, showing A/B = 1.000 and A/B = 0.991, was studied as a function of pH to determine the isoelectric points (IEPs). Figure 5 shows for A/B = 1.000 a gradual increase of the IEP from pH 7.5 to pH 10.0 after decrease of the calcination temperature from 1200° to 900°C. For A/B = 0.991 only a shift of the IEP from pH 7.5 to 8.5 was observed.

The zeta potential of BCTZM with A/B = 1.000 was generally found smaller than that of A/B = 0.991. A different dispersion behavior can be thus expected for BCTZM powders showing different A/B ratios and calcination temperatures.

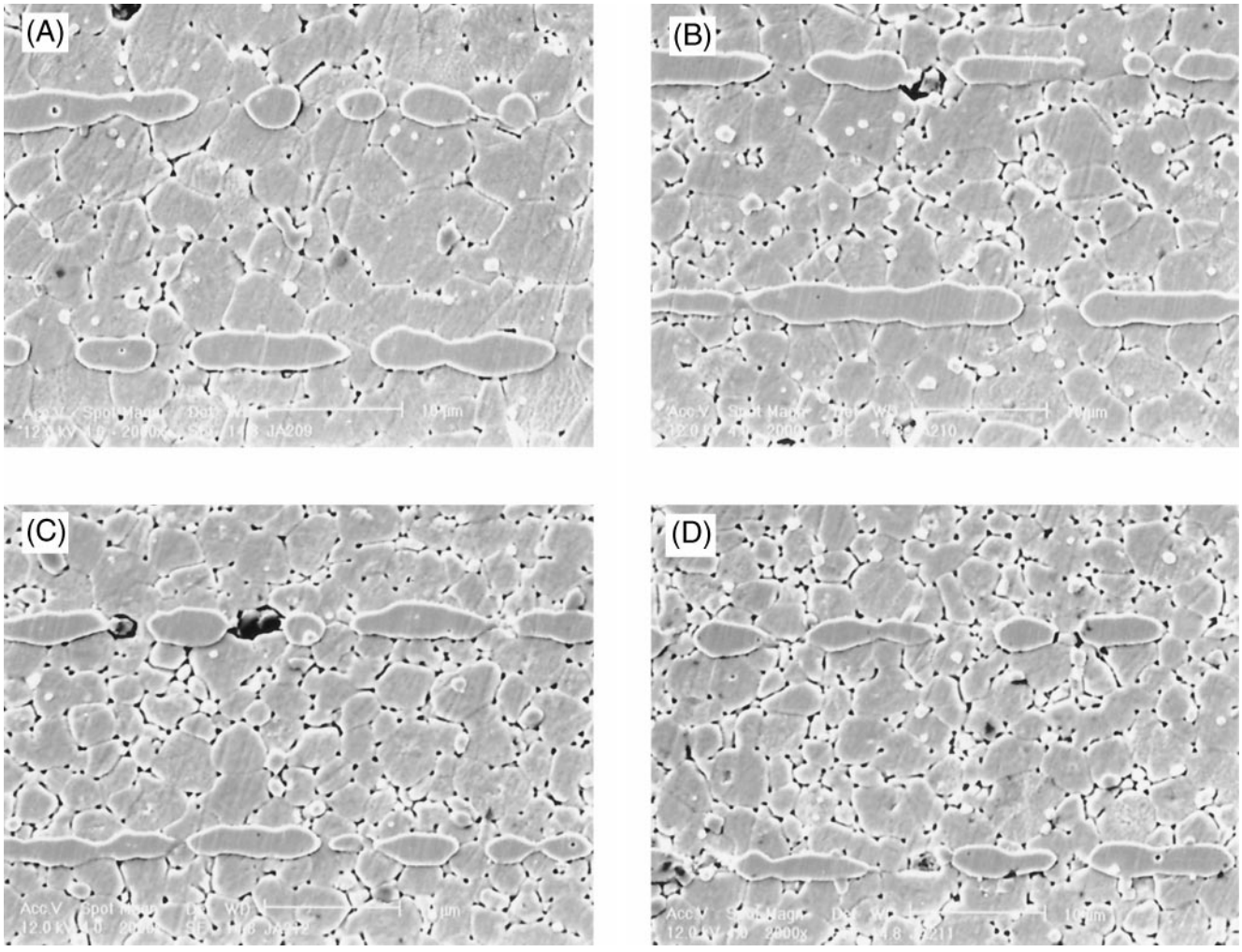

Fig. 3. Microstructure of MLCCs of BCTZM showing A/B = 1.000 ± 0.0015, calcined at 900° (A), 1000° (B), 1100° (C), and 1200°C (D); cofired for 2 h with Ni electrode at 1300°C in 99/1 N_2/H_2 at $p_{O_2} \approx 10^{-14}$ bar.

The colloidal stability of BCTZM powder dispersions could be ascertained by sedimentation experiments, using a solution of ammonium polyacrylate as dispersant which had a molecular weight of 4000. For these experiments powder suspensions showing a solid content of 60 wt% were used to fill tubes of 50 cm length. The dispersant concentration must not exceed a certain limit, because otherwise destabilization occurs, due to electric double layer compression[7] by electrolytic species in the solution. Therefore, a dispersant concentration of 0.8 wt% was chosen in our experiments. Samples calcined at lower temperature showed the most rapid setting. The powder with A/B = 1.000 calcined at 900°C typically accomplished sedimentation within 30 min, while samples calcined at higher temperature did not exhibit significant sedimentation in this time. Increasing sedimentation times, i.e., stabilization of the slurry, were observed for both B/A ratios with increasing calcination temperature.

Figure 6 depicts the measured sedimentation heights of BCTZM slurries as a function of the calcination temperature. The sedimentation volume decreased with increasing calcination temperature. BCTZM powders showing A/B = 0.991, however, always had the highest packing density. The most stable dispersion also had the smallest sedimentation volume and thus the highest particle packing density.

(5) Green Density and Fired Density

MLCC dummies were fired (without electrodes) for 2 h at 1300°C in a moist atmosphere of 99/1 N_2/H_2. The green and fired densities of these dummies were plotted as a function of the calcination temperature in Figs. 7 and 8. For materials showing A/B = 1.000 the green and fired densities both increased with the calcination temperature, while in the case of A/B = 0.991 only the green density was influenced by the calcination temperature. Thus, for A/B = 0.991 the final density can be considered as almost independent of the green density.

The A/B ratio critically influences the development of the microstructure of $BaTiO_3$-based dielectrics. Small excess of TiO_2 leads to formation of $Ba_6Ti_{17}O_{40}$ second phase.[8] The liquid eutectic $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ affects the sintering behavior and enhances grain growth,[9,10] as can be seen in Fig. 4 by the larger grain size of MLCCs with A/B = 0.991. In the case of A/B = 1.000 ± 0.0015 negligible amounts of eutectic melt are present, so that a low green density also leads to a low fired density.[11]

The densification rates of BCTZM with A/B = 1.000 and A/B = 0.991, calcined at various temperatures, were found to be quite different (Figs. 9 and 10). For A/B = 1.000 the maximum shrinkage rate shifts to lower temperatures with increasing calcination temperature. Thus, for calcination at 900°C the maximum shrinkage rate lies at 1300°C, while for a calcination temperature of 1200°C the maximum shrinkage rate is at 1180°C. For Ti-rich powders showing A/B = 0.991 the maximum shrinkage is almost independent of the calcination at ≈1180°C. This effect can be considered as characteristic of a liquid-phase sintering mechanism.

IV. Conclusions

The conclusions drawn from the experimental results are as follows:

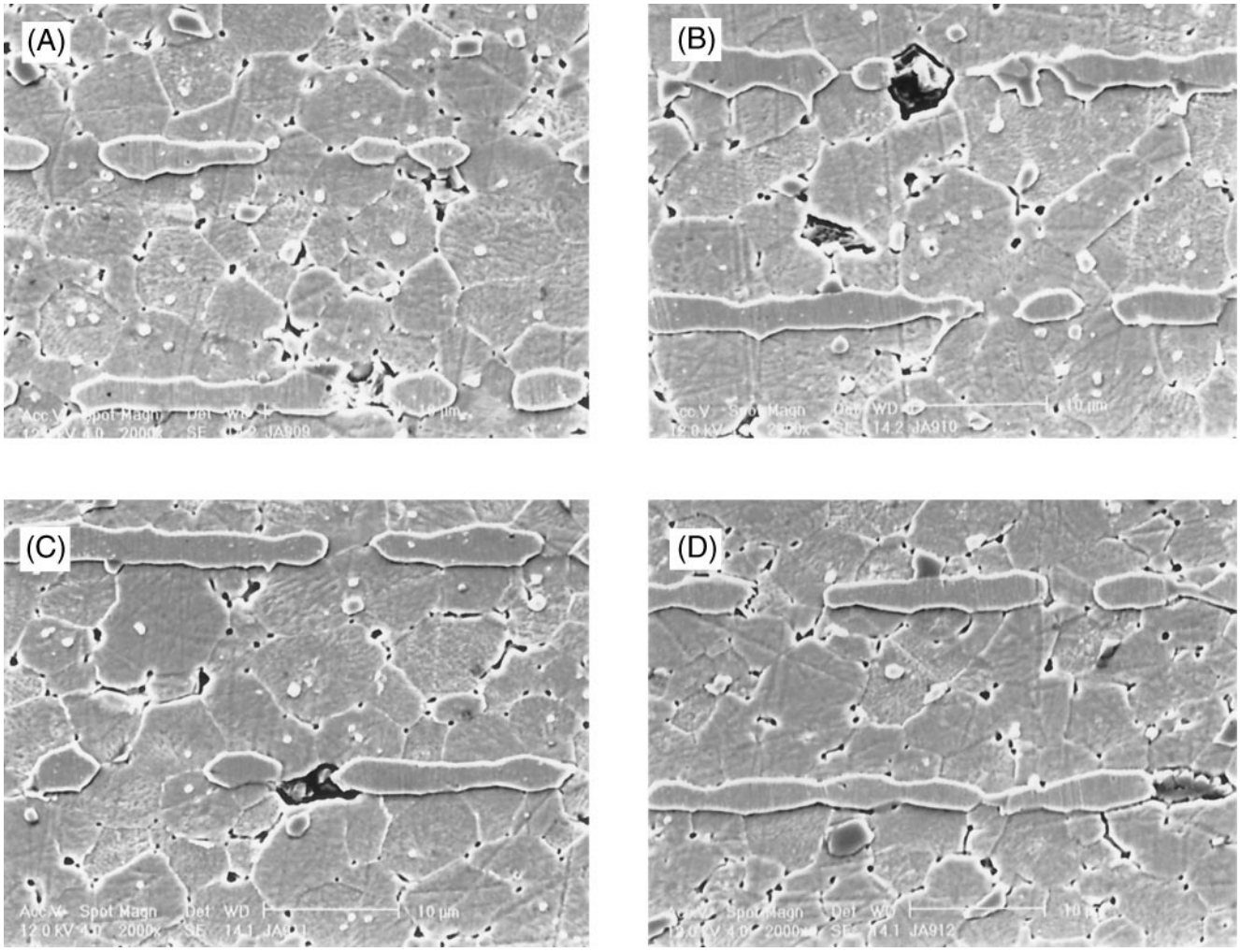

Fig. 4. Microstructure of BCTZM with A/B = 0.991 ± 0.0015, calcined at 900° (A), 1000° (B), 1100° (C), and 1200°C (D) and cofired for 2 h with Ni electrodes at 1300°C in 99/1 N_2/H_2 at $p_{O_2} \approx 10^{-14}$ bar.

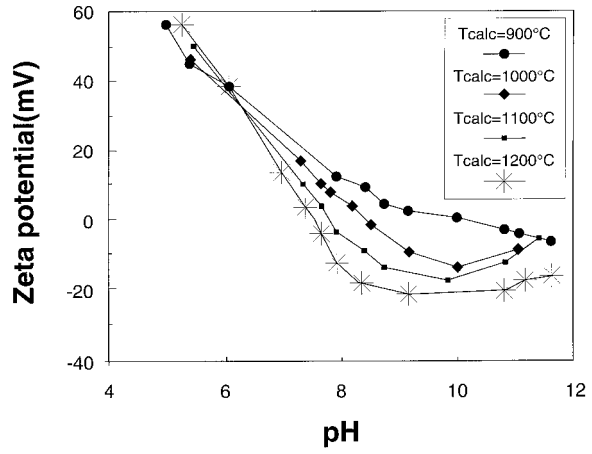

Fig. 5. Electrophoretic mobility as function of pH at various calcination temperatures for BCTZM with A/B = 1.000 ± 0.0015.

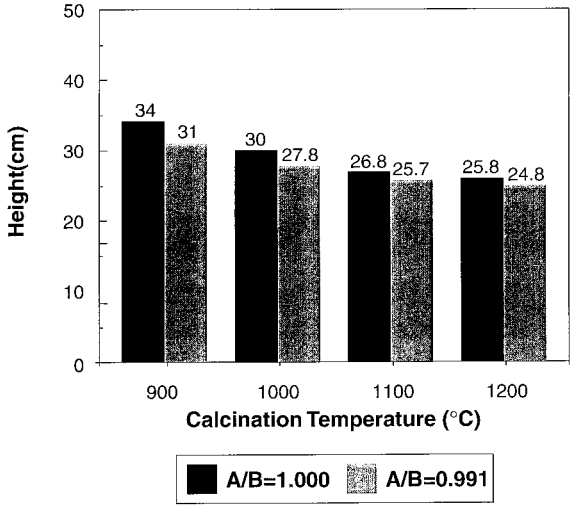

Fig. 6. Comparison of the sedimentation height of aqueous BCTZM slurries, containing 0.8 wt% ammonium polyacrylate dispersant, for A/B = 1.000 ± 0.0015 and A/B = 0.991 ± 0.0015 at various calcination temperatures.

- The effect of calcination temperature on RC, breakdown voltages (V_{bd}), and lifetime was observed only in BCTZM showing A/B = 1.000 ± 0.0015, forming none or negligible amounts of liquid phase during sintering.
- In materials forming liquid eutectic phase (A/B = 0.991 ± 0.0015), the calcination temperature has a minor effect on RC, V_{bd}, and lifetime.
- In materials forming no liquid eutectic phase (A/B = 1.000), the final density, RC, V_{bd}, and lifetime are closely related to the green density.
- The green density is attributed to the colloidal stability of BCTZM powder dispersions. The colloidal stability of BCTZM

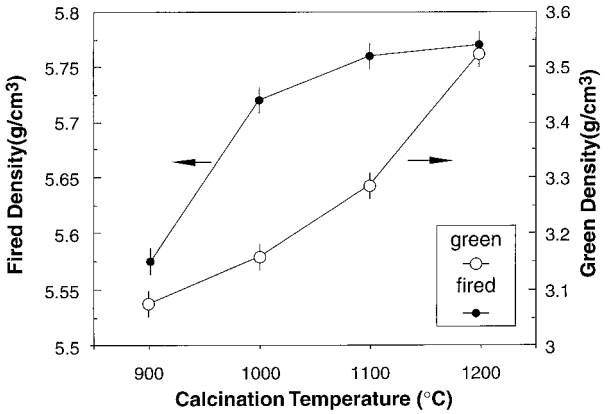

Fig. 7. Green and fired densities as a function of calcination temperature for BCTZM with A/B = 1.000 ± 0.0015.

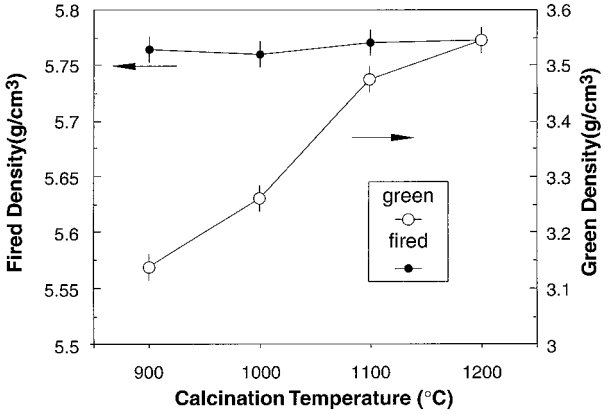

Fig. 8. Green and fired densities as a function of calcination temperature for BCTZM with A/B = 0.991 ± 0.0015.

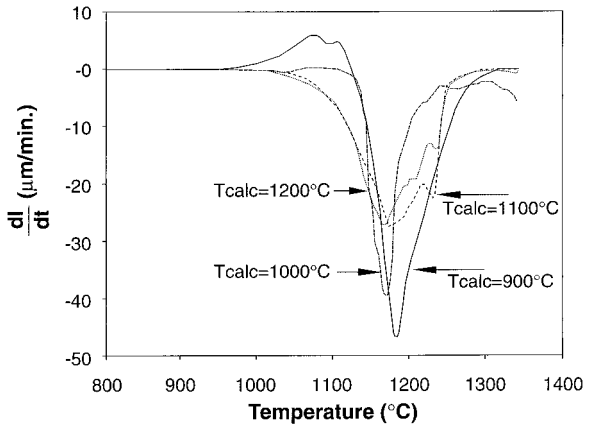

Fig. 9. Densification rate of BCTZM with A/B = 0.991 ± 0.0015, calcined at various temperatures.

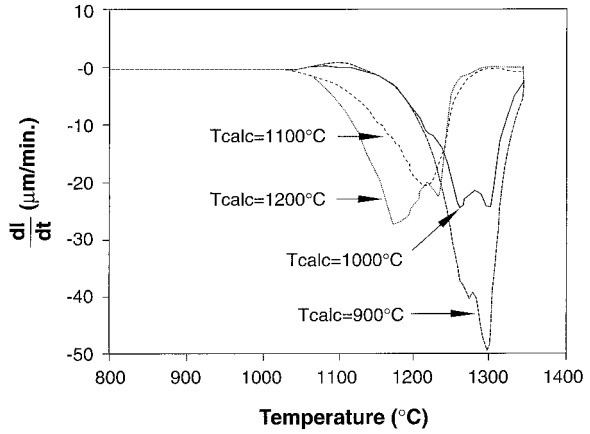

Fig. 10. Densification rate of BCTZM with A/B = 1.000 ± 0.0015, calcined at various temperatures.

and the density of powder packing in aqueous dispersions increase with the calcination temperature.

- The green density is of minor importance for the final density and electrical performance of materials, forming TiO_2-rich liquid eutectic phase during sintering (A/B = 0.991).

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