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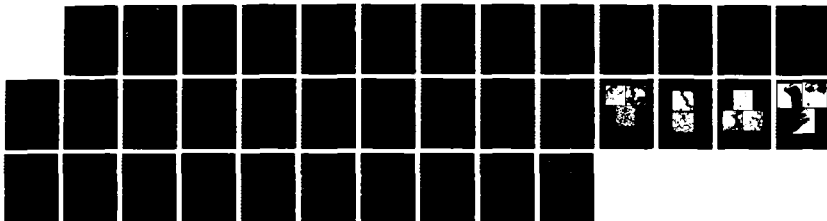
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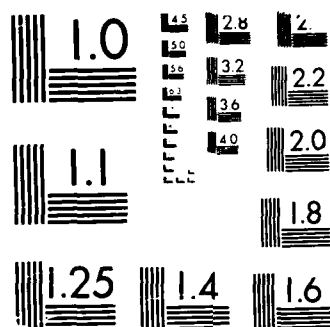
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PROCESSING AND ADDITIVE EFFECTS OF ZrO_2
ON MICROSTRUCTURE AND DIELECTRIC PROPERTIES
OF $BaTiO_3$ CERAMICS

by

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December 1987

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ABSTRACT

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> Dielectric properties and structure of BaTiO_3 ceramics have been shown to be significantly influenced by small additions ($< 2 \text{ wt\%}$) of ZrO_2 . (SEM) and (TEM) observations revealed enhanced microstructural uniformity and retarded grain growth with ZrO_2 addition, depending on sintering temperature (T_s). For $T_s < 1320^\circ\text{C}$, TEM analysis showed ZrO_2 at the grain boundaries as discrete particles ($\sim 0.03 \mu\text{m}$) in a bandwidth of $\pm 50 \text{ \AA}$. Above 1320°C , diffusion of ZrO_2 from the grain boundary region was observed, resulting in increased grain size and a tetragonal structure. X-ray diffraction analysis revealed a pseudo-cubic structure below 1320°C with both twinning and domain structure also suppressed. Ceramics with the pseudo-cubic structures showed a flattened dielectric constant response with temperature and significantly lower dielectric loss.



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PROCESSING AND ADDITIVE EFFECTS OF ZrO_2 ON MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF BaTiO_3 CERAMICS

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I. INTRODUCTION

Ceramic capacitive components typically must have high permittivity for volumetric efficiency and a low temperature coefficient of capacitance for circuit performance. These capacitors are based primarily on ferroelectric compounds such as BaTiO_3 , in which the desirable dielectric characteristics are obtained by incorporation of isovalent or aliovalent additives into the perovskite lattice as substitutions. In small concentrations, substitutions such as NiO , ZrO_2 , Dy_2O_3 and Nb_2O_5 ^{1,2} may also act as grain growth inhibitors. These oxides modify the ferroelectric properties by controlling grain size and by suppressing or broadening the Curie peak. The Curie peak may be equally affected if substantial chemical inhomogeneity exists in the sintered material.³

Zirconia has been shown by Brajer⁴ and Kulscar⁵ to increase the orthorhombic-tetragonal transition temperature in BaTiO_3 while slightly lowering the tetragonal-cubic transition. Hennings et al.⁶ also noted this phenomenon and found that the permittivity increased to a broad maxima as the phase transition points con-

verged. Verbitskaia et al.⁷ found that BaZrO₃ additions to BaTiO₃ had an effect on BaTiO₃ similar to ZrO₂ in that it decreased the axial ratio (c/a) of the tetragonal phase, in agreement with results by Kell and Hellicar.⁸ Similar reductions, in the axial ratio have been achieved by additions of rare earth elements to BaTiO₃.^{9,10} In contrast, Molokhia and Issa¹¹ found that ZrO₂ additions increase the lattice parameters of BaTiO₃,¹² with essentially no effect on the axial (c/a) ratio. Additionally, they observed that the dielectric constant exhibited a nonlinear behavior at low ZrO₂ concentration, while the dielectric losses decreased with increased ZrO₂ content. The nonlinearity of the dielectric constant has been attributed to the presence of Zr⁴⁺ at interstitial positions at low zirconia concentrations, and on Ti⁴⁺ sites at higher concentrations. Maurice¹³ was able to prepare dense ceramic bodies from oxalate derived barium titanate which showed a flattened dielectric response to ZrO₂ additions ≤ 2.0 wt%. This behavior was attributed to ZrO₂ particulate accumulation at the grain boundaries. Armstrong and Buchanan¹⁴ further determined that ZrO₂ resided primarily at the grain boundaries at sintering temperatures less than 1320°C.

Miller¹⁵ and Kahn¹⁶ have shown that grain growth in BaTiO₃ can also be inhibited by incorporation of additives such as carbon and niobium. Miller observed a variation in sintered density as a function of additive content. Kinoshinto and Yamaji¹⁷ showed that as the grain size decreased the permittivity of the material increased and a general broadening of the transition peak resulted. Martirena and Burfoot¹⁸ went a step further and suggested that the room temperature permittivity should markedly

increase when the transition region is suppressed. However Arlt et al.¹⁹ showed that this was not always the case. In a recent study, Arlt showed that the room temperature permittivity decreased when the transition region became suppressed. Additionally, they determined from high angle x-ray analysis, as did Kahn¹⁶, that the degree of tetragonality decreased with grain size, giving rise to a pseudo-cubic structure at room temperature.

The objective of this investigation was to examine the effect of small additions of ZrO_2 on the microstructure, dielectric properties and in particular the grain boundary structure of $BaTiO_3$. The work described here relates to unstabilized ZrO_2 additions, primarily under sintering conditions where solid solubility was not fully achieved, assuring grain boundary residence of the additive.

II. EXPERIMENTAL PROCEDURE

(1) Sample Preparation

This study utilized commercial $BaTiO_3^+$ of high purity with Ba/Ti atomic ratios of 0.997, 1.000 and 1.002, as determined by x-ray fluorescence analysis. The $BaTiO_3$ powders were ball milled (ZrO_2 media) with 0.0-2.0 wt% unstabilized ZrO_2^{++} additions. The average initial particle size of the $BaTiO_3$ and ZrO_2 powders was $1.0\mu m$ and $0.03\mu m$ respectively. Milling was carried out for 12h in a solution of 60 vol% isopropyl alcohol-deionized water

+ Ticon-HPB TAM Ceramics Inc., Niagara Falls, NY.

++ Zircar Products, Inc., Florida, NY.

with 1 wt% Menhadden fish oil⁺⁺⁺ added as a dispersant. Additions of PVA and Carbowax, 1 wt% each, were then made, followed by further milling (1.5h). The slurry was spray dried and the resulting powder uniaxially pressed into discs 16mm x 2mm at 136 MPa. Samples were sintered on ZrO₂ setter plates in air from 1275° to 1350°C for 1-3h. Densities of sintered compacts were measured both geometrically and by He pycnometry.

(2) Characterization

After sintering, some compacts were crushed to an average particle size <40 μ m to achieve optimal random orientation for x-ray diffraction analysis. Diffraction analysis was carried out on the high angle (400)(004) and (200)(002) peaks, to determine the degree of tetragonality.¹⁹ For dielectric measurements, the compacts were mechanically thinned with 600 grit SiC to achieve plane parallel surfaces, upon which Al electrodes were evaporated. Capacitance and loss measurements were made using an automatic capacitance bridge* at 1 and 10 KHz. Bias field measurements (0-300 v/cm) were made with an external high voltage power supply** in series with the capacitance bridge.

SEM microstructural examination were performed on as-fired and fracture surfaces sputtered with Pd-Au, using an ISI DS-130 electron microscope. Specimens for TEM/STEM (Philips EM 400 and 420/Vacuum Generators HB5) were prepared by mechanical

+++ Werner G. Smith Inc., Cleveland, Ohio

* Model 4276A, Hewlett-Packard Co., Palo Alto, CA.

** Model 241, Keithley Instrument Co., Cleveland, Ohio

polishing, using 15 μ m diamond grit and 6 μ m diamond paste, to a thickness of 120 μ m. The samples were further thinned and dimpled on both sides. Foils for TEM/STEM analysis were produced by ion beam thinning to perforation.

III. RESULTS AND DISCUSSION

Addition of monoclinic ZrO₂ (0.5-2.0 wt%) to BaTiO₃ was found, in general, to decrease the density of the sintered compacts. Figure 1 shows the densities to increase with sintering temperature (T_s) up to ~1320°C where maximum density was achieved for samples containing 0 and 2 wt% ZrO₂. For samples with 1 wt% added ZrO₂ maximum density (~96%) was achieved at 1310°C. At higher sintering temperatures, $T_s > 1320^\circ\text{C}$, the densities for all samples decreased. This decrease has been attributed to increased inter-grannular porosity resulting from discontinuous grain growth at higher temperatures as described by Burke.²⁰

The effects of ZrO₂ additions on the microstructure of BaTiO₃ are compared in the SEM photomicrographs of as-sintered surfaces (Figure 2) for samples sintered at 1320°C/2h. With no additive to BaTiO₃ (Figure 2a), a dense microstructure was observed consisting essentially of large grains (avg. GS ~50 μ m), with small grains distributed along the grain boundaries and intersections. With 1.0 wt% ZrO₂ addition (Figure 2b) the fraction of large grains decreased significantly, resulting in a bimodal distribution of large grains in a fine grain matrix. With 2.0 wt% ZrO₂ addition, a dense microstructure consisting entirely of uniform

small grains (avg. GS $\sim 1.0\mu\text{m}$) was obtained. Figure 3 shows an identically similar trend for BaTiO_3 samples sintered at $1300^\circ\text{C}/2\text{h}$, except that here only 1.0 wt% ZrO_2 was needed to suppress the grain growth.

Figure 4 shows the progression of microstructural development (1.0 wt% ZrO_2 added to BaTiO_3) as a function of sintering temperature from 1310 – 1350°C for a 2h soak time. The SEM photomicrographs show uniform grain size structures for the 1310°C and 1350°C samples with significantly larger grain size for the latter. In contrast, the intermediate temperature at 1320°C showed a transition bimodal structure again consisting of large grains in a fine grain matrix. It is clear that the addition of ZrO_2 to BaTiO_3 suppresses grain growth. However, increasing amounts of ZrO_2 (0.5–2.0 wt%) were needed for the suppression of grain growth as the sintering temperature increased from 1300 to 1350°C , indicating progressive solubility of ZrO_2 in the BaTiO_3 lattice.

TEM analysis of BaTiO_3 with added ZrO_2 revealed the presence of ZrO_2 along the grain and pore boundaries for $T_s \leq 1310^\circ\text{C}/2\text{h}$, (1.0 wt% ZrO_2) as shown in Figure 5a. The ZrO_2 appeared as discrete particles ($\sim 0.03\mu\text{m}$), which corresponded to the initial particle size of the added ZrO_2 . However, distribution along the boundaries was not uniform. EDS analysis of these boundary regions revealed a Zr bandwidth of $\pm 50\text{\AA}$ in samples containing 1 wt% ZrO_2 and sintered at 1300°C . As shown in Figure 6, the Zr bandwidth increased to $\sim \pm 100\text{\AA}$ at 1310°C . In contrast, TEM evaluation of samples sintered at 1320°C and 1350°C (1.0 wt% ZrO_2) showed only small discrete regions of ZrO_2 at the grain boundaries and at triple points (Figures 5b, 5c). For the

1350°C sample, the approximate particle size of the residual ZrO_2 was found to be about 90Å, and a broader, less defined Zr bandwidth was observed. The diminished concentration of inter-grannular ZrO_2 particles along with its smaller size and wider bandwidth indicated diffusion of Zr into the BaTiO_3 lattice at $T_s \geq 1320^\circ\text{C}$, leaving insufficient residual ZrO_2 to inhibit grain boundary motion. Interestingly, this is also the approximate temperature for the formation of a liquid phase in the BaTiO_3 system, evident also along grain boundaries in Figure 5. This condition would aid solubility and material transport.

The large grains evident in Figures 2 to 5, typically showed a well developed domain structure with frequent twinning. Detailed analysis of the microstructure by TEM/STEM revealed a reduction in the formation of $\langle 111 \rangle$ twins as the grain size decreased, due either to the presence of ZrO_2 or to a decrease in the sintering temperature. However, the presence of zirconia at the grain boundaries did not significantly disrupt or alter the existing domain structure of the grains (Figure 5a,5b). This may be due to the small amount of ZrO_2 present at the grain boundaries and to limited Zr^{4+} diffusion into the lattice. However, as the grain size decreased the domain structure also decreased with the grains tending to be single domains.

High angle x-ray diffraction analysis of the samples showed progve development of a pseudo-cubic structure as a function of added ZrO_2 , reduced sintering temperature and smaller grain size. At grain sizes $>5\mu\text{m}$ in undoped BaTiO_3 the axial ratio (c/a) was measured to be 1.011. Upon addition of ZrO_2 the axial ratio decreased to 1.005 for samples of comparative grain size. As the

grain size decreased to $0.7\mu\text{m}$ at $T_s=1300^\circ\text{C}$, the pseudo-cubic structure, characterized by two broad reflections centered at $100.9^\circ 2\theta$, with no distinct splitting in the (400)(004) peaks, became fully developed (Figure 7). Table 1 shows this data and the lattice parameter changes for different ZrO_2 concentrations and sintering temperatures. The pseudo-cubic structure modification was also found to be particularly well developed for the optimally dense and small grain size samples with 1.0 wt% ZrO_2 ($1310^\circ\text{C}/2\text{h}$) and 2.0 wt% ZrO_2 ($1320^\circ\text{C}/2\text{h}$).

The observed trends in grain size and x-ray data are in agreement with previous studies.^{7,8} For $T_s=1350^\circ\text{C}$ it is apparent that the added ZrO_2 causes a decrease in the axial ratio of BaTiO_3 , which can be attributed to the incorporation of ZrO_2 into the BaTiO_3 lattice. However, for $T_s<1350^\circ\text{C}$, ZrO_2 acts increasingly as a grain growth inhibitor, decreasing grain size and distorting the perovskite lattice depending on concentration. The formation of the pseudo-cubic perovskite structure, therefore, is an effect of the decreasing grain size as described by Arlt.¹⁹

Dielectric data as a function of temperature for the BaTiO_3 samples (0-2.0 wt% added ZrO_2 , $T_s=1320^\circ\text{C}/2\text{h}$) are presented in Figure 8. Room temperature permittivity values are seen to increase with added ZrO_2 (relative to the undoped BaTiO_3) except for samples with 1.0 wt% ZrO_2 which showed a decrease in permittivity. This is probably due to the highly bimodal microstructure of the 1.0 wt% ZrO_2 sample, compared to the more uniform grain size microstructures depicted in Figure 2. As expected, the smaller grain size microstructures (2.0 wt% added ZrO_2) showed the highest permittivity values,¹⁷ with a near complete suppression of

the Curie peak for the tetragonal-cubic transition at $\sim 125^{\circ}\text{C}$. In contrast, samples with lower ZrO_2 concentration showed a fully developed tetragonal structure as indicated by the sharp Curie peaks. $\tan\delta$ values showed an essentially linear decrease with temperature for both 2.0 and 0.5 wt% added ZrO_2 except for the existence of small transition peaks in the latter sample. For the 1.0 and 0.0 wt% ZrO_2 samples the transition peaks were more pronounced but $\tan\delta$ was less than 4% at room temperature. Both $\tan\delta$ and dielectric constant showed clearly the expected increase in the orthorhombic-tetragonal and corresponding decrease in the tetragonal-cubic transition temperatures.^{5,6} This is another indication that ZrO_2 is going into solid solution in the BaTiO_3 at 1320°C . Figure 9 shows the dielectric behavior of ceramics with optimally dense fine grained microstructures obtained at 1310°C and 1320°C , with a 2h soak. The samples show full Curie peak suppression and linear $\tan\delta$, decreasing with temperature. The somewhat higher permittivities and $\tan\delta$ values for the 1320°C sample reflect the higher density and ZrO_2 solubility.

In line with the microstructures shown in Figures 3 and 4, the samples fired at 1300°C showed high permittivities and an essentially flat dielectric response with temperature between room temperature and 120°C as depicted in Figure 10. However, with increased sintering temperature the permittivity values decreased, for the same added ZrO_2 content (1.0 wt%) reflecting progressively larger grain size development and increasing ZrO_2 solubility in the perovskite lattice. The relatively low permittivity for ceramics with $T_s=1350^{\circ}\text{C}$ reflected further the relatively low density

of the sample. Dissipation factor trends were again similar to the trends in Figure 8.

Summarizing the dielectric data for BaTiO_3 with small ZrO_2 additions, it can be concluded that the dominant effect was grain size. With smaller grain size higher permittivities were observed as well as lower dielectric losses. This grain size suppression corresponded to the condition of ZrO_2 being resident at the grain boundaries. In cases where ZrO_2 diffused into the lattice, a shift in the Curie transition peak was observed and also a slight increase in permittivity. These observations are reflected in the data given in Figure 11 which shows the change in capacitance with bias field for the different samples. Ceramics with more uniform, fine grain microstructures generally showed smaller capacitance deviation with applied bias field, indicative also of lower dissipation factors and higher insulation resistance.

Figure 12 shows the stoichiometry effect on the dielectric properties of the doped BaTiO_3 samples. The samples compared were sintered at $1300^\circ\text{C}/2\text{h}$ and had 1.0 wt% added ZrO_2 . These specimens all showed a flattened dielectric response above the orthorhombic-tetragonal transition and a low $\tan\delta$ which decreased linearly with temperature. The samples with atomic ratios <1.000 showed higher permittivity values, this effect being due to the samples having higher density and smaller grain size.²¹ No difference was observed in the dielectric response of samples with atomic ratios >1.000 , within the stoichiometric range examined. The $\tan\delta$ for all three samples was observed to decrease linearly with temperature and showed little significant variation.

IV. CONCLUSIONS

1. Unstabilized (monoclinic) ZrO_2 added to BaTiO_3 (0.5-2.0 wt%, sintered at 1300-1350°C/1-2h) was found to result in:
a) suppression of grain growth with ZrO_2 resident at the grain boundaries and, b) diffusion into the perovskite lattice at higher sintering temperatures, resulting in increased permittivity and convergence of the orthorhombic-tetragonal and tetragonal-cubic transition temperatures.
2. For case (a) the tetragonal-cubic transition peak was suppressed, resulting in an essentially flat dielectric constant profile to room temperature and a linear decrease from 25° to -55°C. Dissipation factor values were much reduced for these samples.
3. Suppression of the Curie peak as described above, coincided with a suppression of the cubic-tetragonal transition resulting in a pseudo-cubic structure characterized by a reduced c/a ratio.
4. Stoichiometry effects of the ZrO_2 addition to BaTiO_3 were relatively insignificant for conditions where the added ZrO_2 was resident at the grain boundaries.

V. Acknowledgments

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Figure 10. Dielectric spectra for BaTiO_3 (1.0 wt% added ZrO_2) samples sintered at 1300, 1310, 1320 and 1350°C for 2h.

Figure 11. Change in capacitance as a function of bias field for BaTiO_3 with 1.0 wt% added zirconia.

Figure 12. Dielectric response of BaTiO_3 (1.0 wt% added ZrO_2) with varying Ba/Ti atomic ratios 0.997, 1.000 and 1.002 sintered at $1300^\circ\text{C}/2\text{h}$.

TABLE I. EFFECT OF ADDED ZIROCNIA ON THE AXIAL RATIO OF BaTiO₃

SAMPLE	PEAK	a(Å)	c(Å)	c/a
BaTiO ₃ (Ba/Ti=0.997)	(200,002)	3.009	4.038	1.011
PLUS ZrO ₂ (1300°C/1h)				
0.5 wt%	(400,004)	NO SPLITTING*		
1.0 wt%	(400,004)	NO SPLITTING		
2.0 wt%	(400,004)	NO SPLITTING		
(1310°C/2h)				
0.5 wt%	(400,004)	NO SPLITTING		
1.0 wt%	(400,004)	NO SPLITTING		
(1320°C/2h)				
1.0 wt%	(400,004)	3.993	4.009	1.004
2.0 wt%	(400,004)	NO SPLITTING		
(1350°C/1h)				
1.0 wt%	(400,004)	3.992	4.010	1.005
2.0 wt%	(400,004)	4.005	4.025	1.005

* Indicates pseudo-cubic modification

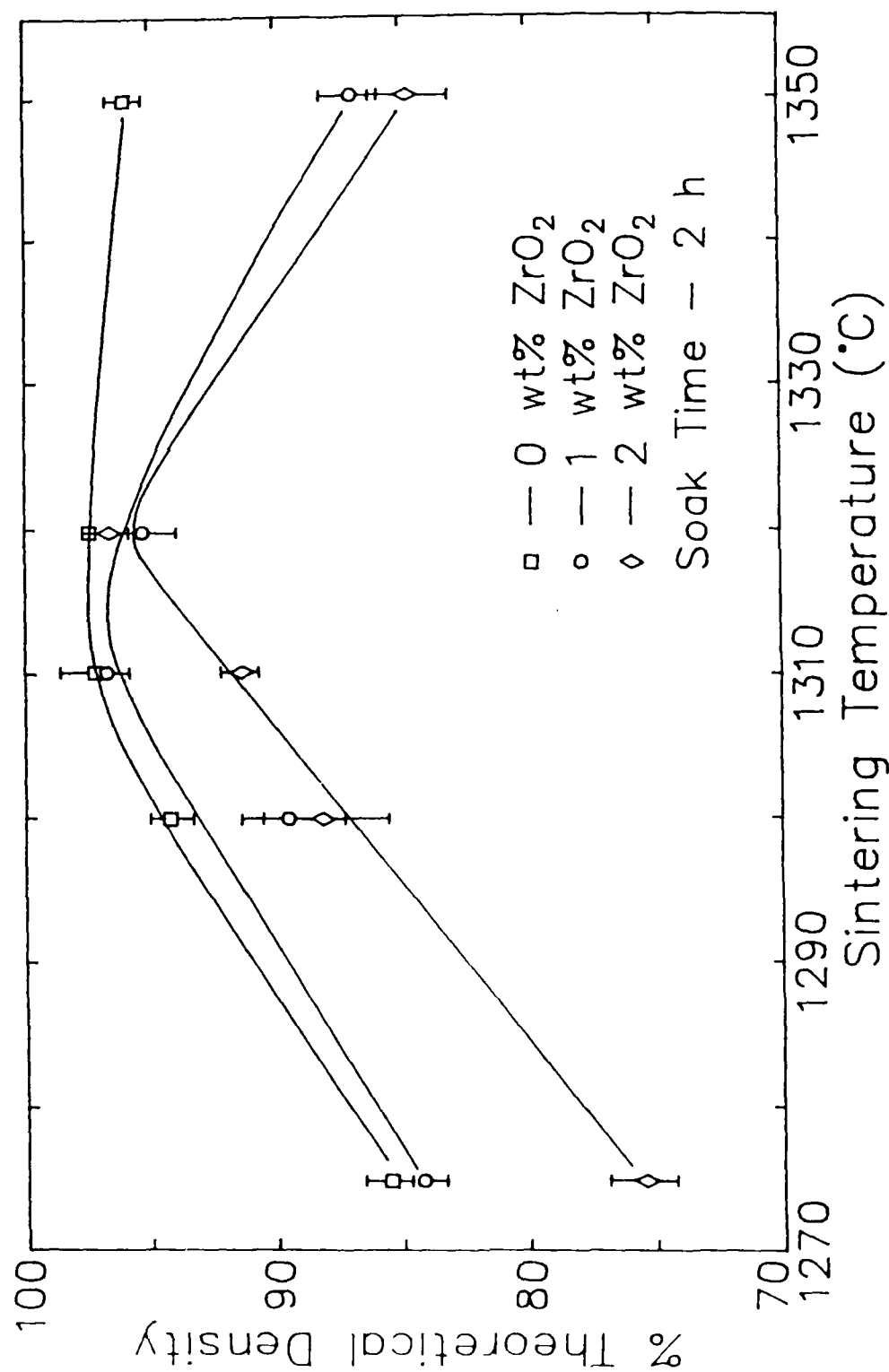


Figure 1. Fired density (%ThD) as a function of sintering temperature for BaTiO_3 modified with 0-2.0 wt% monoclinic ZrO_2 .

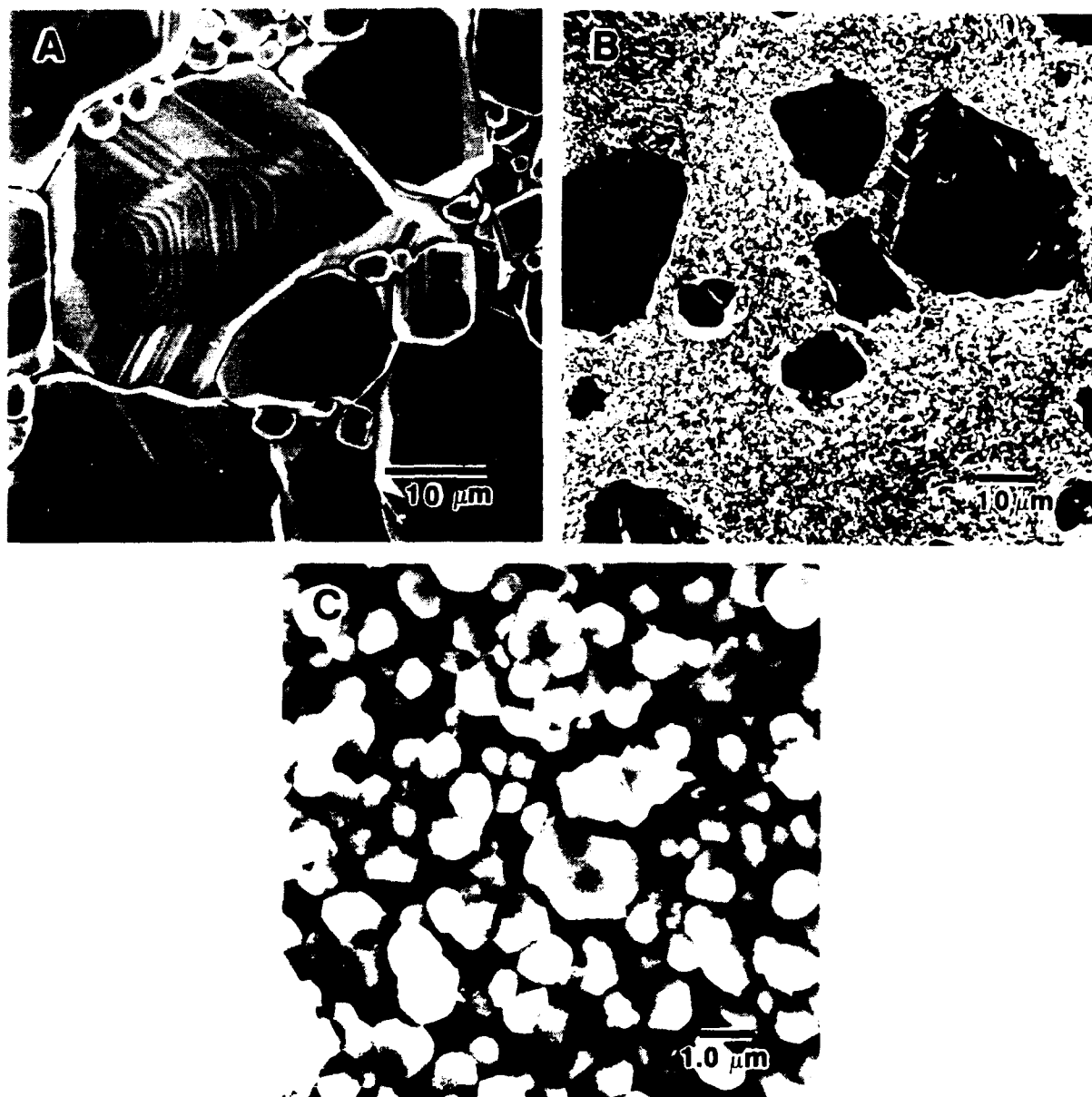


Figure 2. The effect of added monoclinic zirconia on grain size for BaTiO_3 ($\text{Ba}/\text{Ti}=0.997$) samples sintered at $1320^\circ\text{C}/2\text{h}$: a) 0.0 wt% added ZrO_2 , b) 1.0 wt% and c) 2.0 wt%.

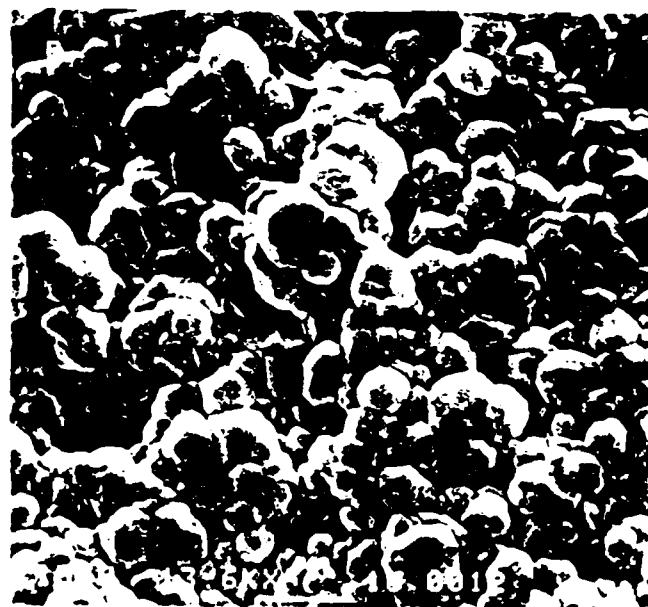
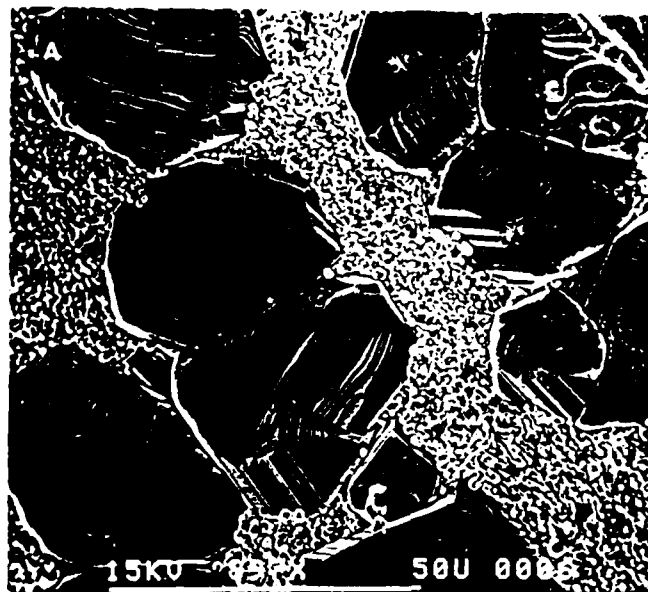


Figure 3. Effect of added zirconia (1.0 wt%) on grain size inhibition of BaTiO_3 ($\text{Ba/Ti}=1.002$) sintered at $1300^\circ\text{C}/2\text{h}$: a) 0.0 wt% added ZrO_2 and b) 1.0 wt% ZrO_2 .

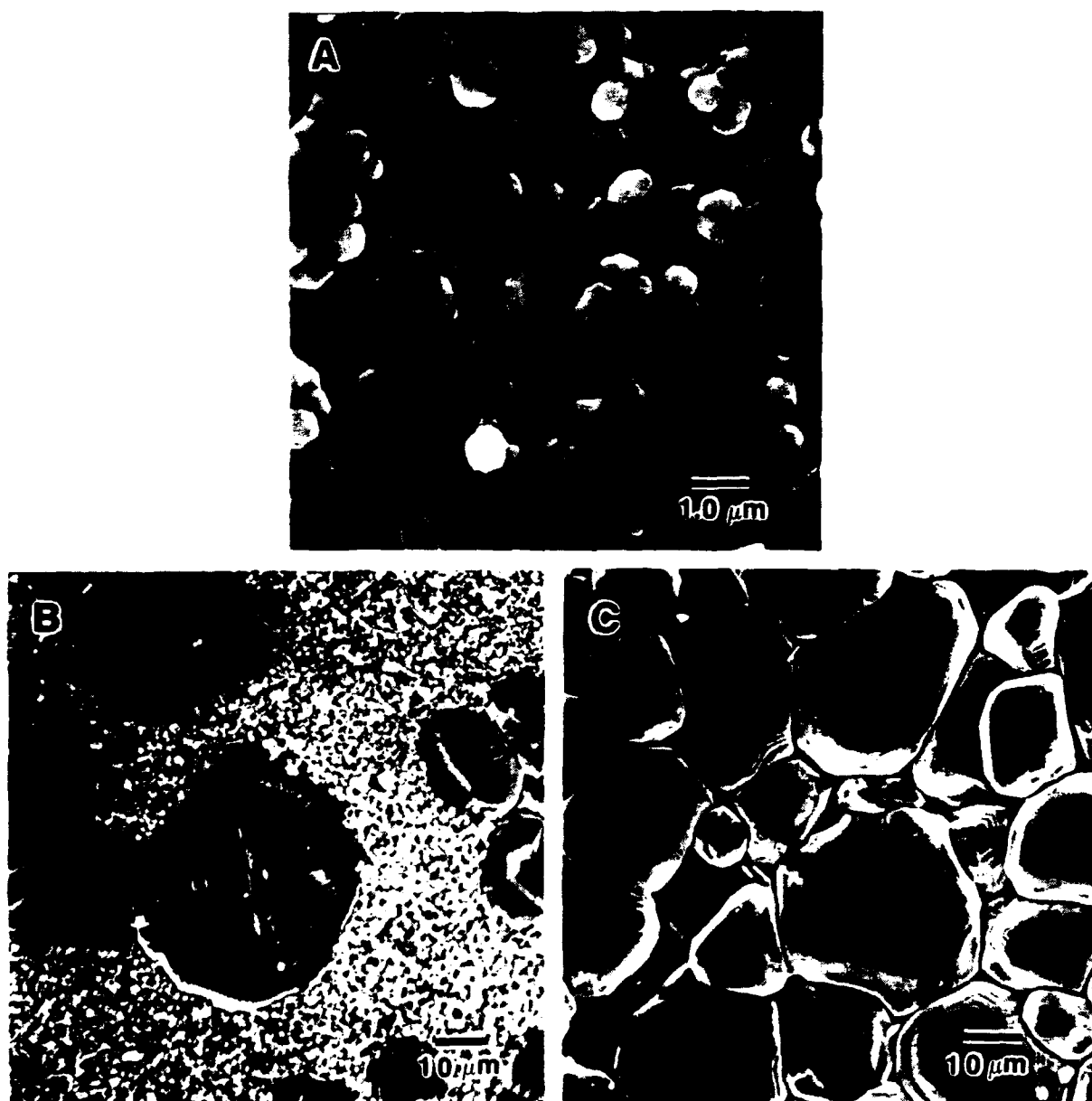


Figure 4. The effect of sintering temperature on densification and microstructure of BaTiO₃ (Ba/Ti=0.997) samples with 1.0 wt% ZrO₂: a) 1310°C/2h, b) 1320°C/2h and 1350°C/2h.

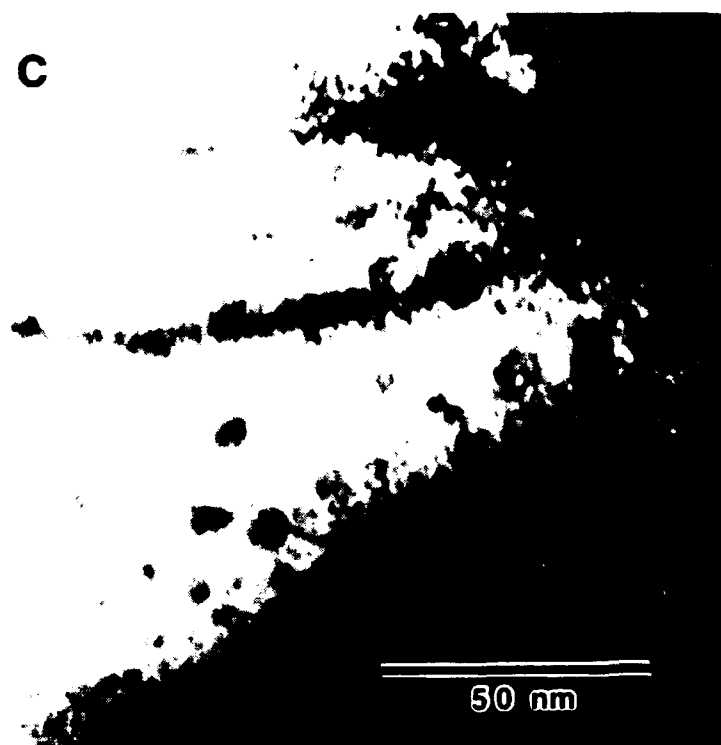
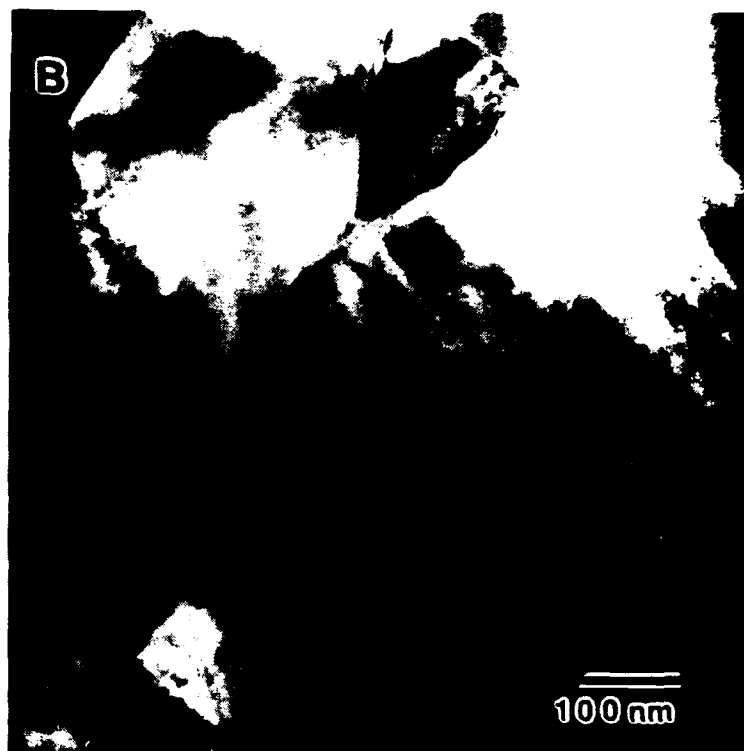
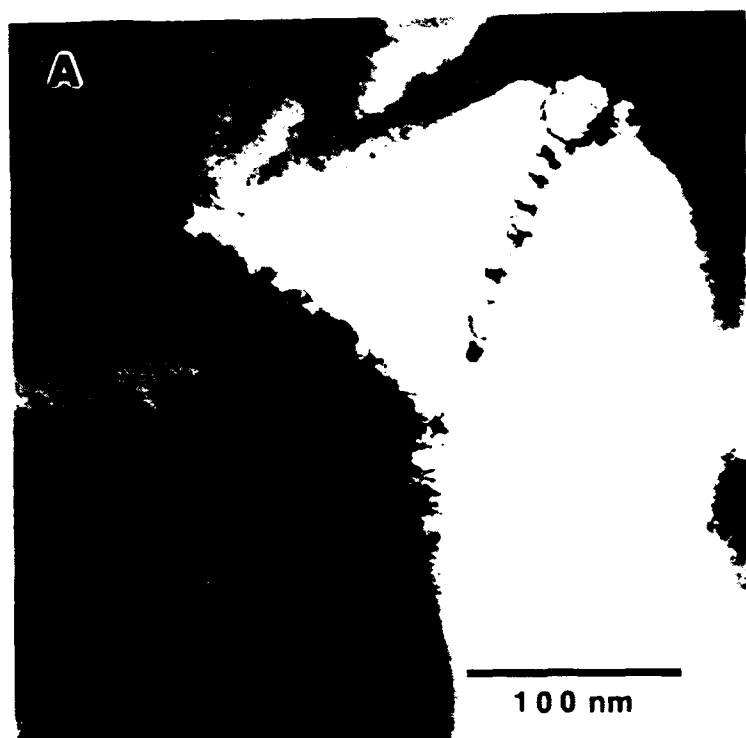
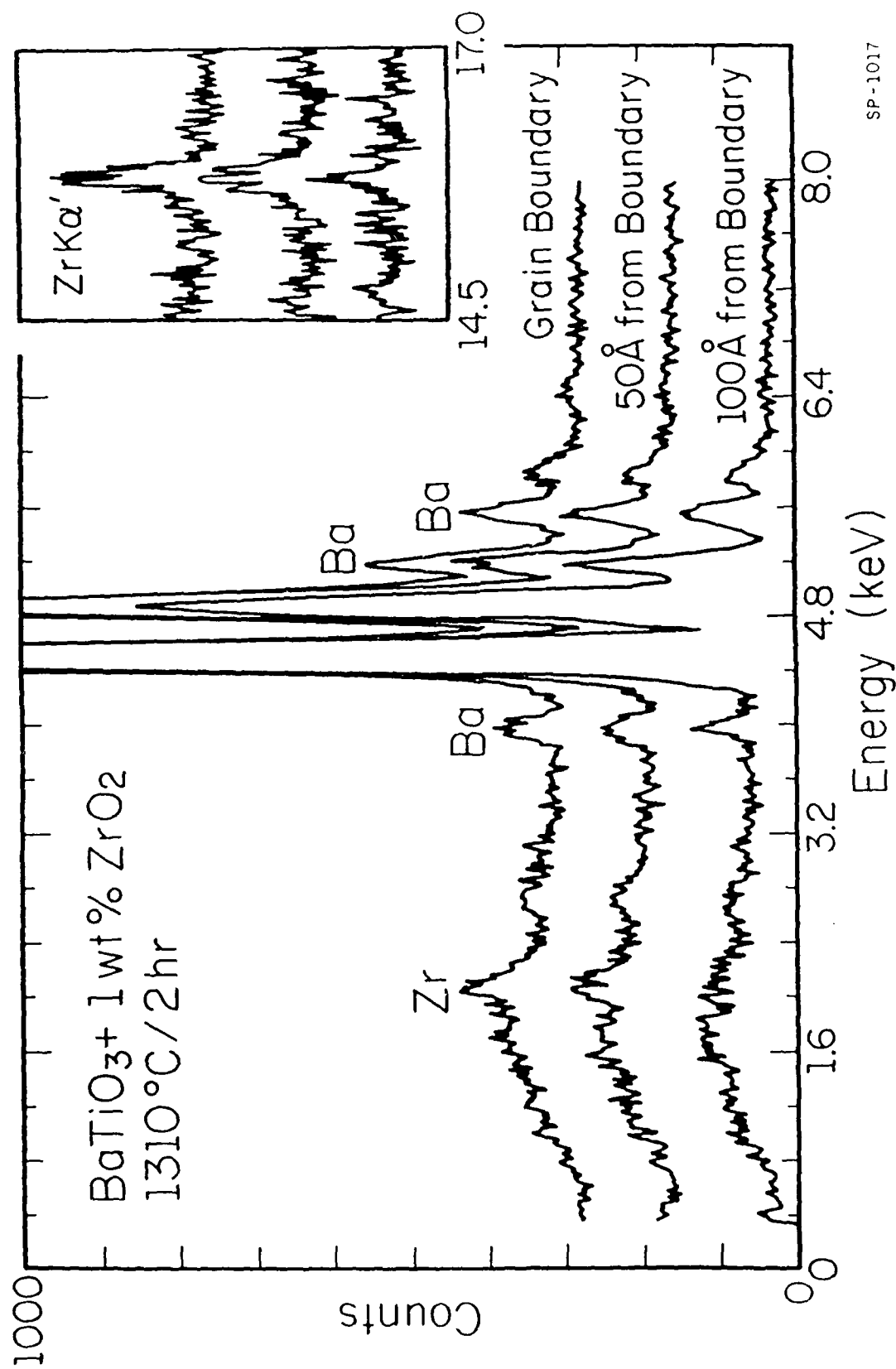


Figure 5. TEM photomicrographs showing progressive dissolution of ZrO_2 (1.0 wt%) along BaTiO_3 ($\text{Ba/Ti}=0.997$) grain boundaries with increasing sintering temperature: a) $1310^\circ\text{C}/2\text{h}$, b) $1320^\circ\text{C}/2\text{h}$ and c) $1350^\circ\text{C}/2\text{h}$.



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Figure 6. EDS profile of grain boundary region in BaTiO₃ (1.0 wt% added ZrO₂) sintered at 1310°C/2h, showing Zr distribution around grain boundary.

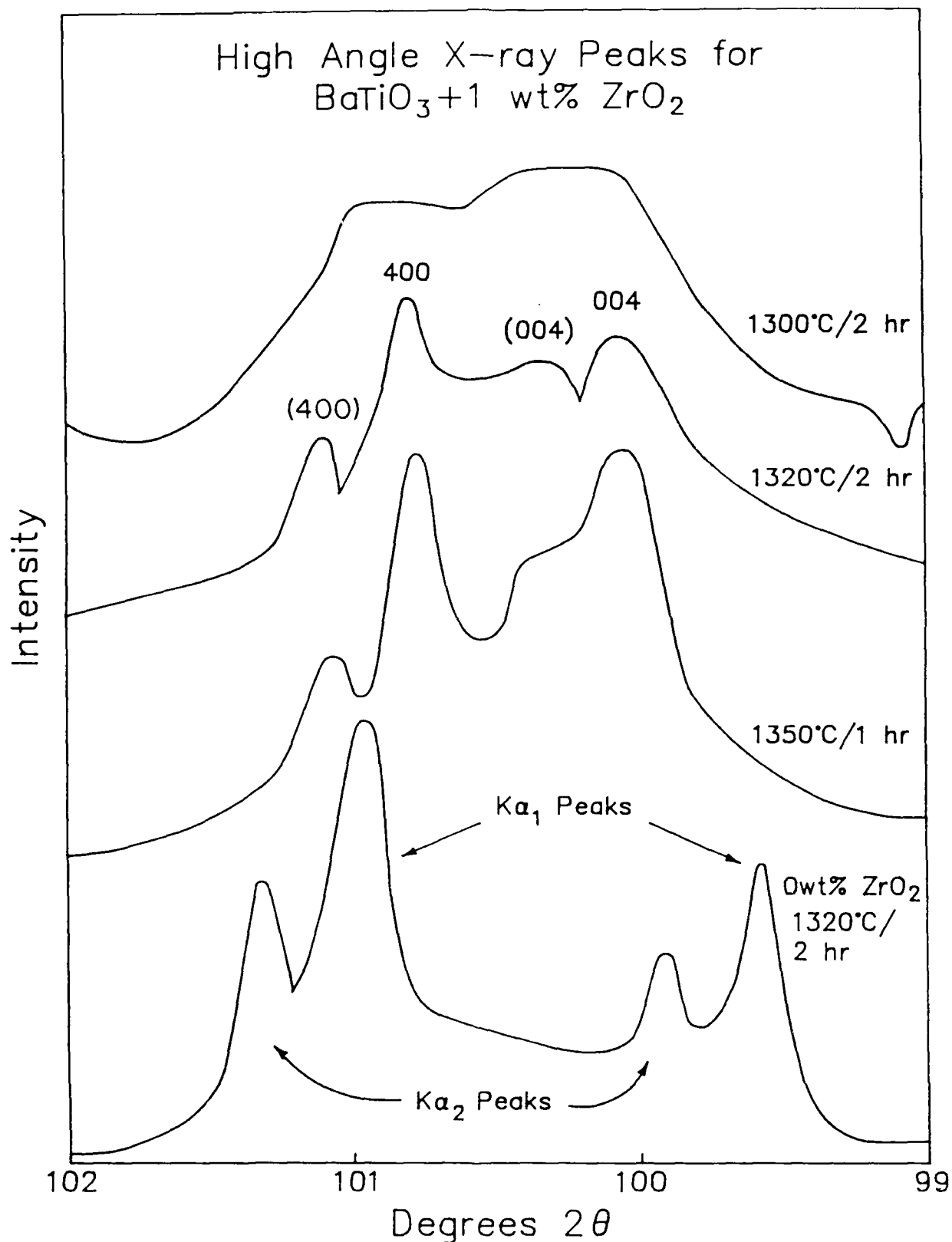


Figure 7. High angle x-ray diffraction pattern of BaTiO_3 with 1.0 wt% ZrO_2 showing progressive suppression of the tetragonal (400) and (004) peaks as sintering temperature is decreased.

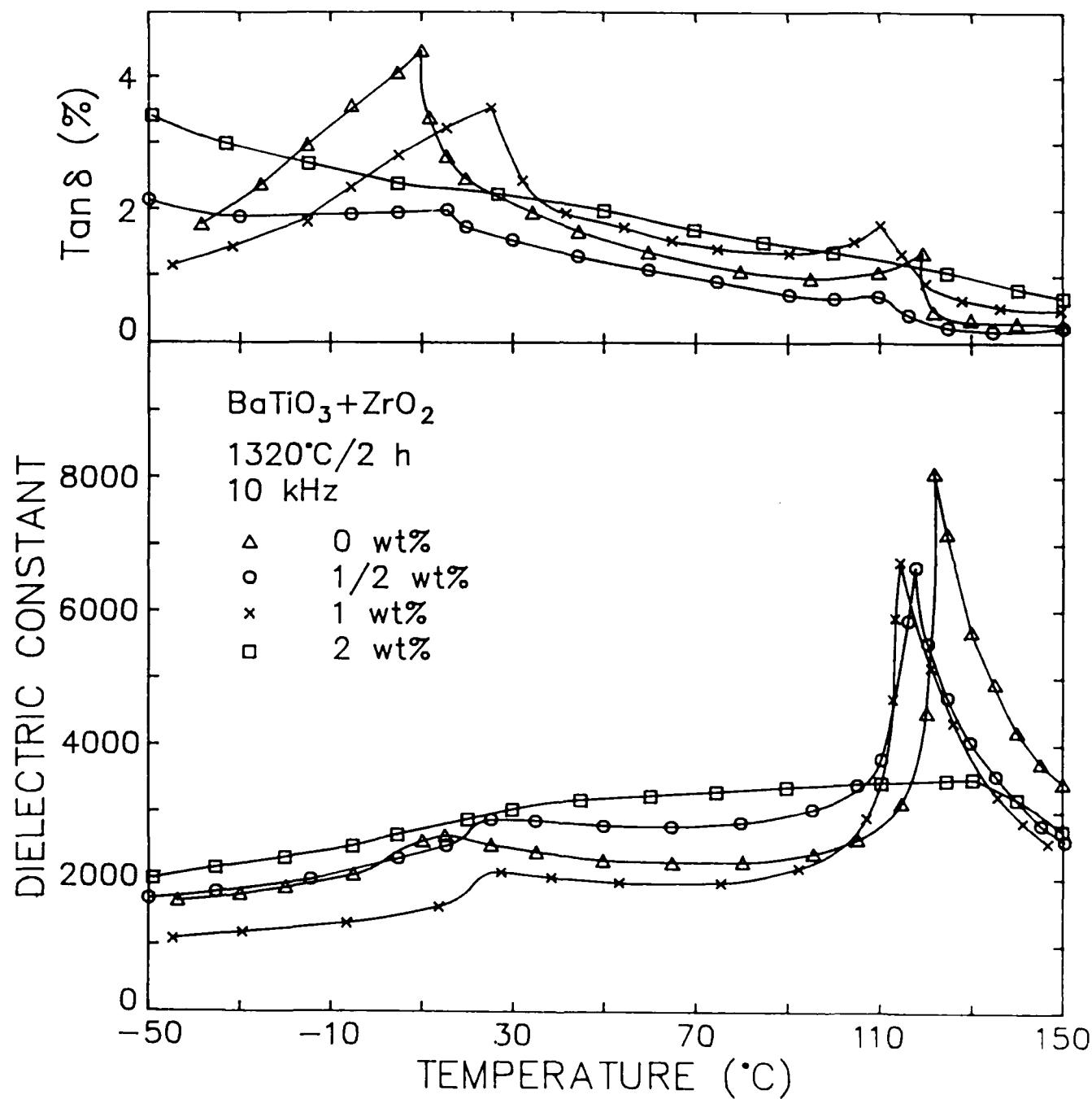


Figure 8. Dielectric response of 0.0, 0.5, 1.0 and 2.0 wt% zirconia additions to BaTiO₃ sintered at 1320°C/2h (10kHz).

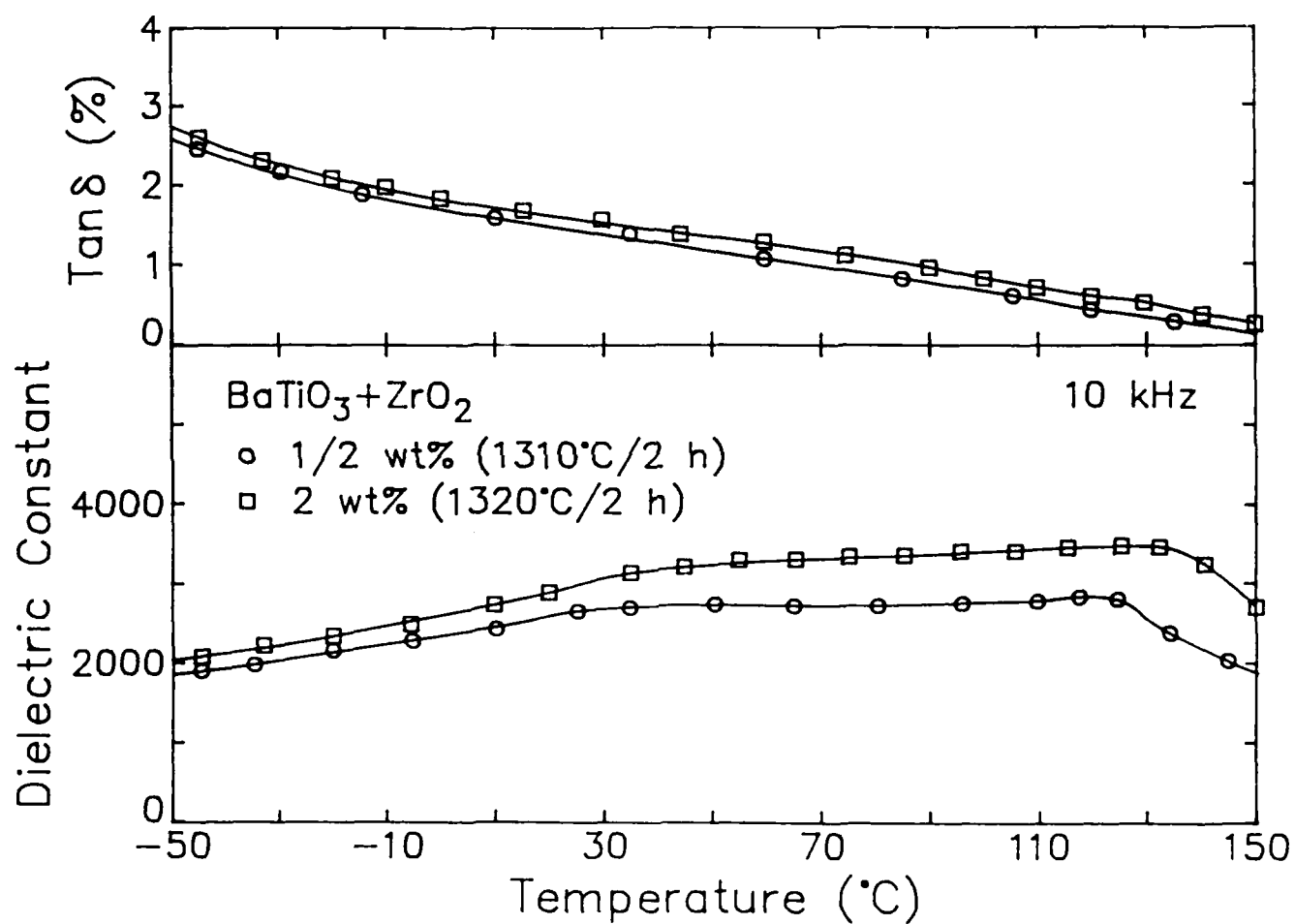


Figure 9. Dielectric response of BaTiO_3 with optimal zirconia concentrations of 0.5 wt% $1310^{\circ}\text{C}/2\text{h}$ and 2.0 wt% $1320^{\circ}\text{C}/2\text{h}$ at 10kHz.

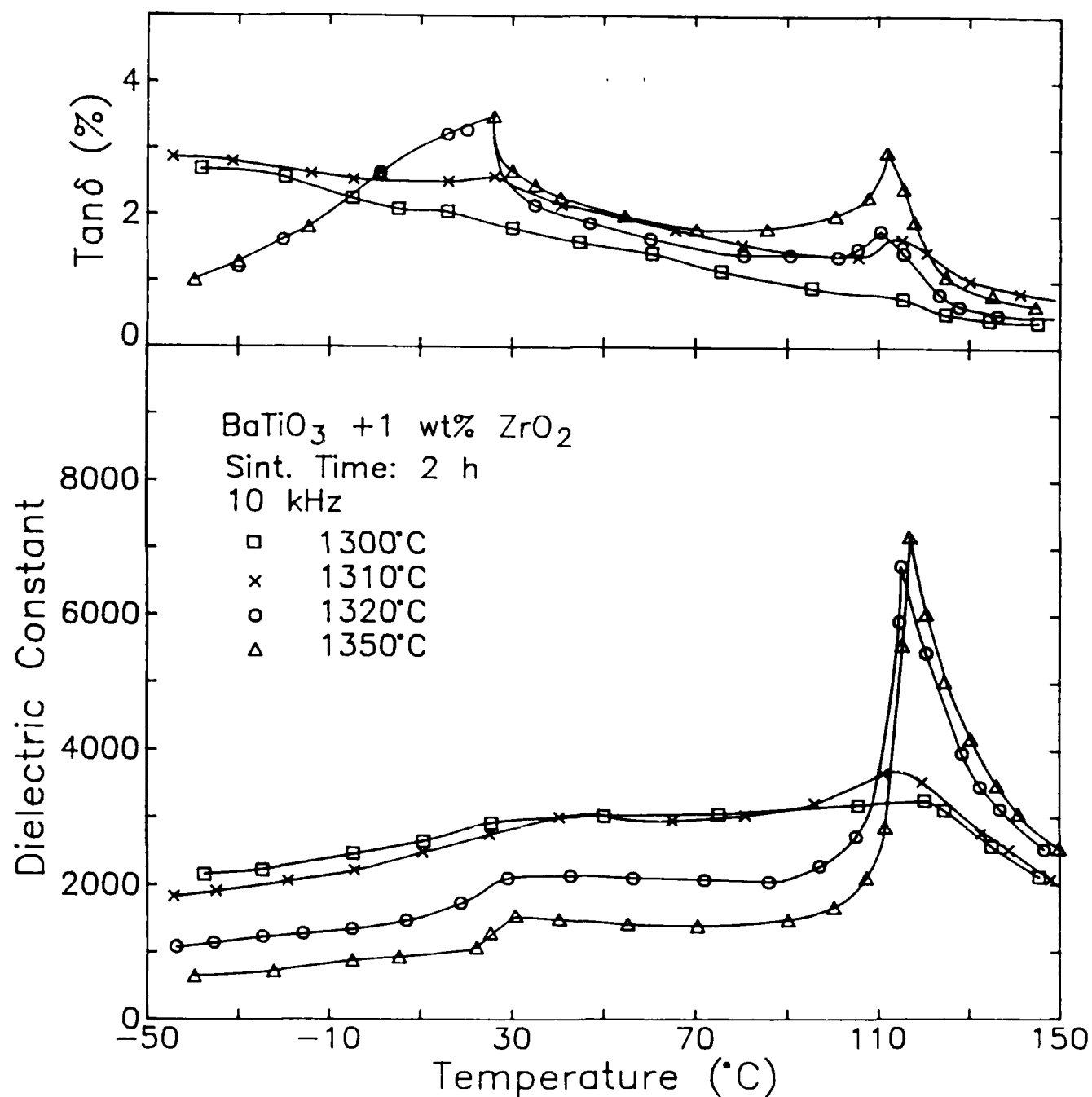


Figure 10. Dielectric spectra for BaTiO_3 (1.0 wt% added ZrO_2) samples sintered at 1300, 1310, 1320 and 1350 $^{\circ}\text{C}$ for 2h.

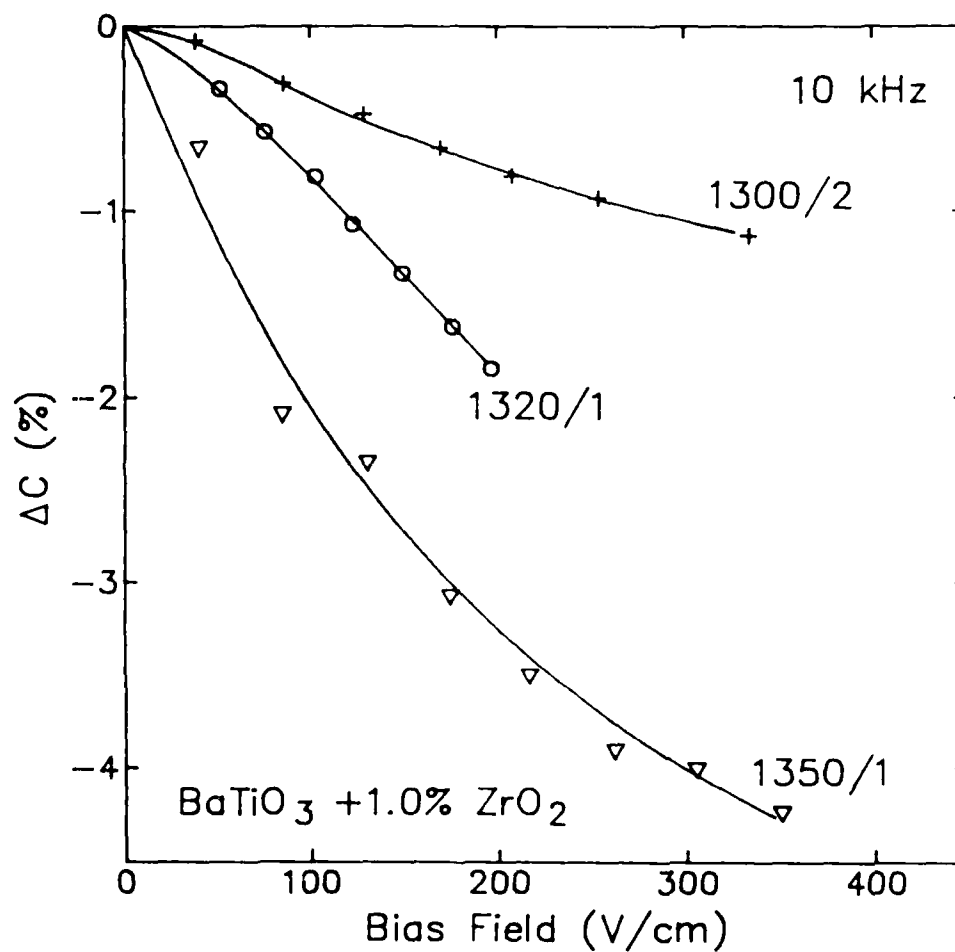


Figure 11. Change in capacitance as a function of bias field for BaTiO₃ with 1.0 wt% added zirconia.

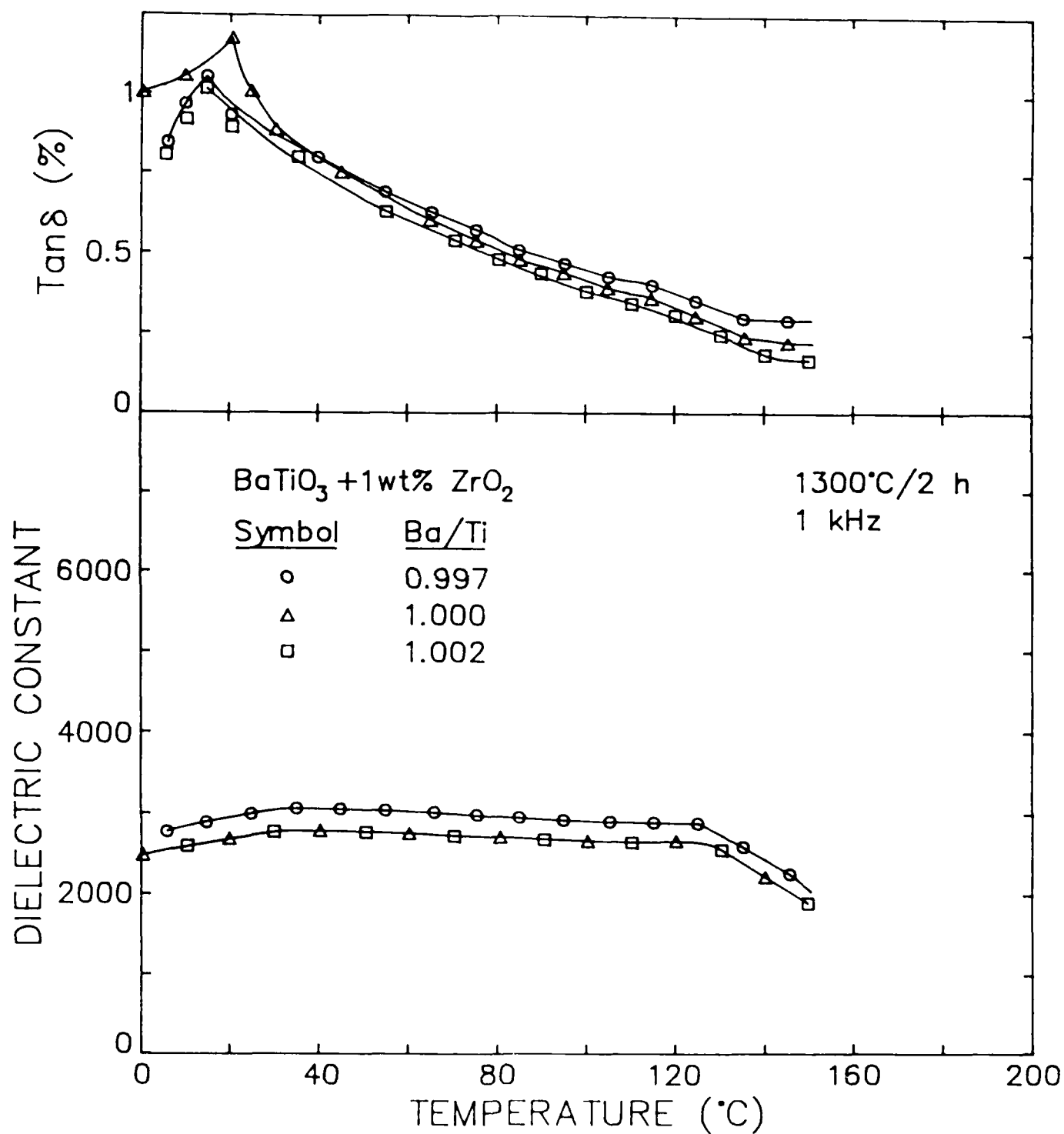


Figure 12. Dielectric response of BaTiO_3 (1.0 wt% added ZrO_2) with varying Ba/Ti atomic ratios 0.997, 1.000 and 1.002 sintered at 1300°C/2h.

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