



Dielectric Properties of Acceptor-Doped (Ba,Ca)(Ti,Zr)O₃ Ceramics

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Abstract. The dielectric properties of (Ba,Ca)(Ti,Zr)O₃ ceramics containing various acceptor and donor dopants on the B sites have been studied. Formation of charge compensating “complexes” between acceptors, donors and oxygen vacancies has been observed. All acceptors cause a reduction of the Curie point. The maximum dielectric constant increases with the average grain size almost independent of the acceptor incorporated. Ceramics fired in reductive atmospheres reveal pronounced changes of the dielectric properties after annealing in oxidizing atmosphere. In particular the losses and the maximum dielectric constants are significantly affected by the annealing time, temperature and partial pressure of oxygen.

1. Introduction

Incorporation of heterovalent ions in the perovskite lattice of barium titanate leads to significant changes of the dielectric and ferroelectric properties. Generally, ions with large radius and low valency tend to enter the A (Ba) sites, while ions with small radius and higher valency favor the B (Ti) sites [1]. Ions bringing excess charges into their host lattice are named donor ions, while those bringing a charge deficit are named acceptor ions. Depending on their ionic radius, the trivalent ions of rare earths enter either A sites or B sites. A few of the smaller rare earth ions can enter both A and B sites, depending on the B/A atomic ratio of the perovskite [2]. These ions can therefore act as donors as well as acceptors in barium titanate.

Almost all heterovalent substituents tend to reduce the *c/a* ratio of the tetragonal unit cell and to decrease the ferroelectric Curie point. The presence of acceptors and donors strongly affects the stoichiometry and microstructure of ferroelectric perovskites [3]. The charge deficit of acceptors is usually compensated by doubly ionized oxygen vacancies, $V_{O}^{\bullet\bullet}$ [4,5]. Formation of acceptor-oxygen vacancy complexes give rise to generation of elastic and electric dipoles which have a strong influence on the

dielectric and ferroelectric properties as well as the aging behavior [6].

This investigation deals with the influence of various acceptor-oxygen vacancy and acceptor-donor complexes on the ferroelectric and dielectric properties of reductively fired and oxidizingly aftertreated (Ba,Ca)(Ti,Zr)O₃ (BCTZ). This basic composition has been selected because of its importance for the manufacture of ceramic capacitors and the strong effect of re-oxidation treatment on the dielectric properties.

2. Sample Preparation

Ceramic materials of composition (Ba_{0.96}Ca_{0.04})[Ti_{1-x-y-z}A_xD_yZr_z]_aO_{3-δ} were prepared by standard solid state techniques, using reagent grade raw materials. As acceptors the ions of A = Mg, Al, Ga, Mn, Cr, Sc, Y, Yb have been studied and as donors D = Nb and W. The acceptor and donor concentrations were $x, y \leq 0.01$, while that of Zr was $z = 0.18$ and $a = 0.995$.

Before and after calcination the powders were brought into a fine grained state with particle sizes between 0.5 and 1 μm, using a ball mill with 2 mm Ø Y-stabilized zirconia balls. The major impurities Sr in

BaCO₃ and Hf in ZrO₂ were taken into account at weighing. After 6 h calcination at 1250°C in air single-phase perovskites have been observed in X-ray diffraction analyses.

The fine milled calcined powders were granulated and uniaxially pressed at 4 kbar to green discs of about 0.6 mm thickness and 6 mm diameter. The excess of A-site ions, B/A < 1, required small SiO₂ additives as sintering aid. The predensified green discs were fired for 1 h at 1320°C in a reductive atmosphere of moist (saturated with H₂O at 20°C) N₂, containing 1 vol.% H₂. The partial pressure of oxygen was continuously monitored, using a zirconia cell at 735°C (AMETEK, Pittsburgh). The measured values of Po₂ agreed well with the calculated Po₂ = 2.1·10⁻⁵ Pa. Sintered ceramic samples exhibited densities of 95% to 99% of the theoretical density. Part of the ceramics were aftertreated for 2 h at 1000°C in air (Po₂ = 2·10⁴ Pa) or in an atmosphere of N₂/50 ppm O₂ (Po₂ = 5 Pa). Heating and cooling rates were 300°C/h or 600°C/h.

The average grain sizes d_{av} have been determined from etched ceramics, using the line intercept method and light microscopy. The grain size decreased with increasing acceptor dope concentration. A detailed list of the measured grain sizes is shown in Table 1. Cr/Ni-Au electrodes were applied by evaporation on the sintered ceramic discs. Curie point and dielectric properties were determined at 1 kHz and 1 Vrms in the temperature range -50°C to 150°C. The Curie point, T_C , was determined from the maximum of the dielectric constant ϵ in the dielectric temperature characteristic $\epsilon(T)$. All dielectric samples prepared showed very high insulation resistances $R_I > 10^{12} \Omega \text{cm}$ at 20°C.

3. Experimental Results

3.1. Curie Point Shifts

The Curie point T_C sensitively depends on the kind of acceptor ion on B sites. The T_C shift is determined by the ionic radius as well as the valence state and the ground state of the acceptor ion [7]. Both the acceptor ion and the presence of oxygen vacancies tend to remove locally the tetragonal symmetry and the ferroelectric state, thus leading to a reduction of T_C . The presence of the small Ca content seems not to affect the acceptor concentration for B/A ratios

Table 1. Average grain size and maximum permittivity of reductively fired (1320°C, Po₂ = 2.1·10⁻⁵ Pa) and re-oxidized (1000°C, Po₂ = 5 Pa) (Ba_{0.96}Ca_{0.04})[Ti_{0.82-x}A_xZr_{0.18}]_{0.995}O_{3- δ} .

Acceptor (A)	x	d_{av} (μm)	ϵ_{max}	ϵ_{max}
			reduced	re-oxid.
Mg	0.0025	5.7	15,900	26,250
	0.0050	4.7	11,200	16,700
	0.0075	3.6	9,160	13,610
	0.0100	2.4	6,750	8,800
Al	0.0025	4.4	11,600	16,080
	0.0050	3.3	10,350	15,060
	0.0075	2.8	7,590	10,310
Cr	0.0100	2.6	8,150	10,430
	0.0025	6.1	12,790	26,060
	0.0050	5.4	13,050	15,990
Mn	0.0075	5.0	11,350	12,540
	0.0100	4.1	9,320	9,610
	0.0025	2.9	11,860	13,250
	0.0050	2.6	8,940	10,360
Sc	0.0075	2.5	8,660	7,231
	0.0100	2.4	7,230	7,120
	0.0025	6.7	15,610	28,090
	0.0050	5.9	13,690	24,050
Y	0.0075	4.6	10,550	18,670
	0.0100	3.9	9,800	15,800
	0.0025	7.0	17,390	28,650
	0.0050	5.0	13,180	20,610
Yb	0.0075	3.9	11,120	15,220
	0.0100	3.4	9,970	13,120
	0.0025	7.2	16,950	29,520
	0.0050	5.6	13,140	22,020
	0.0075	4.1	10,140	15,980
	0.0100	3.3	8,910	14,370

≈ 0.995 . Also no Curie point change was obtained for Ca contents < 8 at.%, while (Ca_{Ti})^{''} acceptors strongly reduce T_C [8]. Co-doping with even small amounts of (Nb_{Ti})['] donors leads to semiconductive ceramics after firing in reducing atmosphere. Since the Nb donors have not been compensated by Ca acceptors, we can assume that (Ca_{Ti})^{''} are not present.

Figures 1(a) and 1(b) show the variation of T_C as function of the dopant concentration x for various acceptor ions A = Mg²⁺, Al³⁺, Ga³⁺, Sc³⁺, Y³⁺, Yb³⁺, Mnⁿ⁺ and Crⁿ⁺ in the perovskite phase (Ba_{0.96}Ca_{0.04})[Ti_{0.82-x}Zr_{0.18}A_x]_{0.995}O_{3- δ} . The solid lines in Fig. 1 represent the materials sintered in reductive atmosphere (Po₂ = 2·10⁻⁵ Pa), while the dashed lines represent the same materials aftertreated at Po₂ = 5 Pa. The atomic ratio of A and B site ions was adjusted to B/A = 0.995. Corresponding to B/A < 1 one can be sure that all dopant ions act as acceptors on B sites, i.e., (Mg_{Ti})^{''}, (Ga_{Ti})['], (Sc_{Ti})['], (Y_{Ti})['], (Yb_{Ti})['].

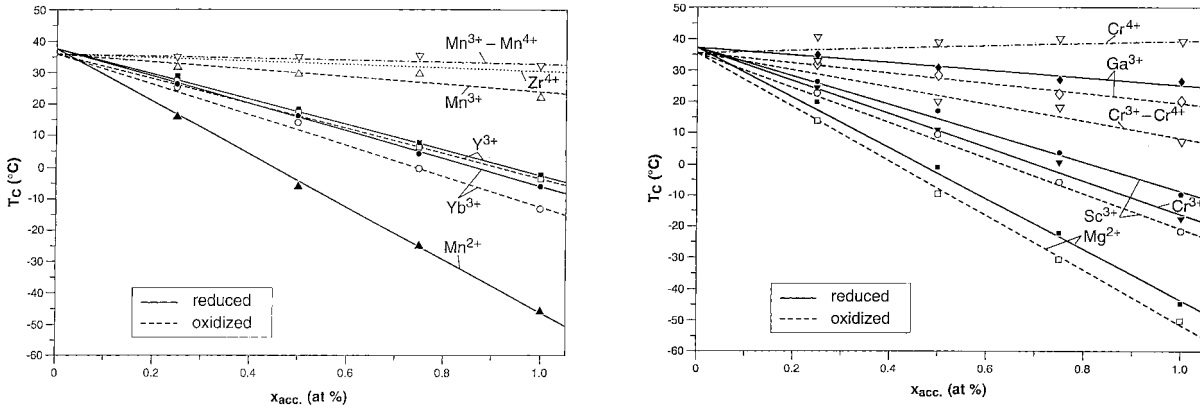


Fig. 1(a), 1(b). Concentration dependence of the Curie point for various acceptor-doped materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})[\text{Ti}_{0.82-x}\text{Zr}_{0.18}\text{A}_x]_{0.995}\text{O}_{3-\delta}$ in the reduced ($\text{Po}_2 = 2 \cdot 10^{-5}$ Pa) and oxidized ($\text{Po}_2 = 5$ Pa) state, represented by the solid and dashed lines, respectively. The dashed-dotted lines for $\text{Mn}^{3+}-\text{Mn}^{4+}$ and Cr^{4+} represent ceramics oxidized in air ($\text{Po}_2 = 2 \cdot 10^4$ Pa).

Former investigations revealed that Mn^{2+} , resp. $(\text{Mn}_{\text{Ti}})''$ is formed in the given reductive atmosphere [4]. Cr^{3+} ions form $(\text{Cr}_{\text{Ti}})'$. The rare earth doped materials exhibit a high insulation resistance and a large T_C shift after reductive firing, thus indicating that Y and Yb have mainly entered the B sites. However, small amounts of rare earth ions on A sites cannot be excluded.

As already expected, all acceptors caused a negative Curie point shift, $\Delta T_C = [T_C(x) - T_C(0)] < 0$. The largest shifts occurred for the divalent ions, yielding for

$$\begin{aligned} \text{Mn}^{2+}, \text{Mg}^{2+}: \quad \Delta T_C(A_{\text{Ti}}^{2+}) \\ \simeq -80^\circ\text{C/at.}\% \text{ in BCTZ-18\%Zr} \end{aligned}$$

This shift compares well with that observed for Ca^{2+} on Ti sites [8]. The shift of the trivalent ions is much lower.

$$\begin{aligned} \text{Cr}^{3+}, \text{Sc}^{3+}, \text{Y}^{3+}, \text{Yb}^{3+}: \quad \Delta T_C(A_{\text{Ti}}^{3+}) \\ \simeq -50^\circ\text{C/at.}\% \text{ in BCTZ-18\%Zr} \end{aligned}$$

For comparison, the Curie point shift for isovalent Zr^{4+} ions is (dotted line in Fig. 1(a)):

$$\Delta T_C(\text{Zr}_{\text{Ti}}^{4+}) = -7^\circ\text{C/at.}\%$$

The large difference in the T_C -shift between ions of different valencies already reflects the important role of the oxygen vacancies on the ferroelectric state. In the case of isovalent Zr^{4+} no oxygen vacancies are formed, so that the ferroelectric state is weakly disturbed and the resulting reduction of T_C is small.

In the case of trivalent substituents, one V_0^{**} is formed for charge compensation of 2 acceptors. Divalent substituents acting as twofold charged acceptors on B sites need one V_0^{**} for charge compensation. Divalent acceptor ions thus give rise to the largest ΔT_C . The presence of one oxygen vacancy together with a lower valent ion on B sites obviously causes a local reduction of c/a in a much larger volume as compared to Zr^{4+} . Similar results were obtained for compositions with a lower Zr content ($y = 0.10$). However, in this case the T_C -shifts were slightly lower.

3.1.1. Re-Oxidation Effects on T_C . The annealing procedure leads to a shift $\delta T_C = (T_{C(\text{ox})} - T_{C(\text{red})})$ of the Curie point. This T_C -shift between the reduced and oxidized state is usually smaller than the compositional shift ΔT_C . The Curie point of the oxidized state $T_{C(\text{ox})}$ was determined in samples annealed for 2 h at 1000°C in $\text{N}_2/50$ ppm O_2 ($\text{Po}_2 = 5$ Pa) (heating and cooling rate: 300°C/h). In the case of valence stable acceptors, e.g., Mg, Y, Sc, Yb the effect of re-oxidation on T_C is expected to be rather small, because the acceptor- V_0^{**} complex should be not affected by the oxidizing heat treatment, except for local rearrangements of oxygen vacancies. A very small δT_C was observed for Mg and Y doped material, as can be seen in Fig. 1. In the case of Sc and Yb doped BCTZ a slightly negative Curie point shift of $\delta T_C = -8^\circ\text{C/at.}\%$ Yb and $-13^\circ\text{C/at.}\%$ Sc has been found.

In contrast to the negative δT_C of ions with fixed valency the Curie point shift turns out to be positive

for Mn and Cr acceptors. This effect is expected because the number of oxygen vacancies is reduced, due to the oxidation of these valence instable ions. TGA analyses have confirmed that under the conditions of reductive firing ($P_{O_2} = 2.1 \cdot 10^{-5}$ Pa, 1320°C) Mn^{2+} is formed, while at 1000°C in an atmosphere of $\text{N}_2/50$ ppm O_2 ($P_{O_2} = 5$ Pa) Mn^{3+} is the prevailing valence state, as can be seen in Fig. 2. At even higher partial pressure of oxygen and lower temperature, e.g., 800°C —air ($2 \cdot 10^4$ Pa), about 50% of the Mn^{3+} are transformed to Mn^{4+} [4]. This leads to a lower ΔT_C as compared to the Zr-doped material (line marked with Mn^{3+} – Mn^{4+} in Fig. 1(a)). In contrast to Mn^{2+} the compositional Curie point shift of Mn^{3+} is rather small, $\Delta T_C(\text{Mn}^{3+}) \simeq -15^\circ\text{C/at.}\%$. This effect is expected, because part of the strained volume is restored with respect to higher c/a ratio, giving rise to a higher T_C . The oxidation of Cr^{3+} leads to comparable results. The dashed lines in Fig. 1(b) marked with Cr^{3+} – Cr^{4+} and Cr^{4+} represent the ceramics annealed in 50 ppm O_2 ($P_{O_2} = 5$ Pa) and in air ($P_{O_2} = 2 \cdot 10^4$ Pa), respectively.

Generally, the level of T_C depends on the annealing temperature T_a , the annealing time t_a and the partial pressure of oxygen. The influence of P_{O_2} and T_a was studied for BCTZ containing Mg, Sc, Cr, Mn and one additional sample containing Mn/W. These materials were annealed for $t_a = 2$ h at various top temperatures T_a in $\text{N}_2/50$ ppm O_2 or air. Heating and cooling rates were 600°C/h . The results are shown for $\text{N}_2/50$ ppm O_2 (dashed lines) and air (solid lines) in Fig. 3. Ions with fixed valency (Mg^{2+} , Sc^{3+}) exhibit the same

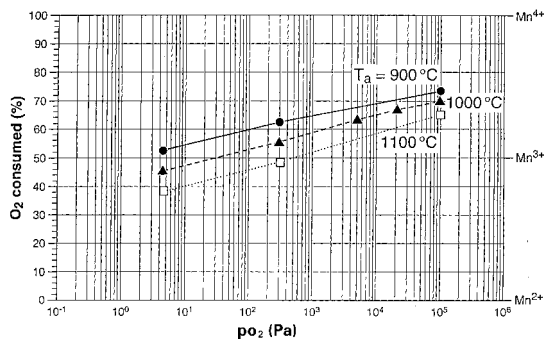


Fig. 2. Oxygen consumption of $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{[Ti}_{0.81}\text{Zr}_{0.18}\text{Mn}_{0.01}]_{0.995}\text{O}_{3-\delta}$, due to valence change of Mn. TG equilibrium measurement as function of the oxygen pressure p_{O_2} various temperatures.

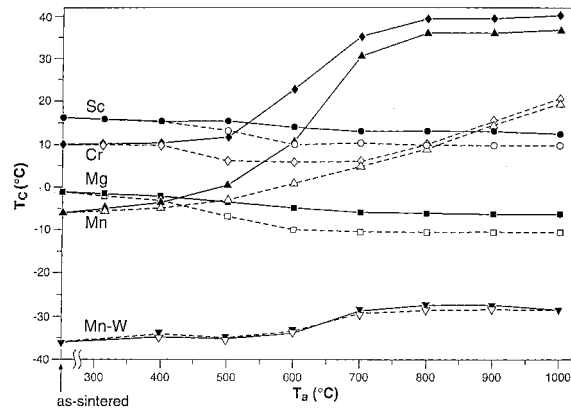


Fig. 3. Variation of the Curie point with the annealing temperature for different acceptor doped materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{[Ti}_{0.815}\text{Zr}_{0.18}\text{A}_{0.005}]_{0.995}\text{O}_{3-\delta}$ with $\text{A} = \text{Cr, Mn, Mg, Sc}$. The lines marked with Mn-W represent a material of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{[Ti}_{0.802}\text{Zr}_{0.178}\text{Mn}_{0.01}\text{W}_{0.0075}]_{0.995}\text{O}_{3-\delta}$. The materials were annealed for 2 h in an oxidizing atmosphere with $P_{O_2} = 5$ Pa (dashed lines) and $P_{O_2} = 2 \cdot 10^4$ Pa (solid lines).

behavior, a slight decrease of T_C at annealing temperatures T_a ranging between $\simeq 500^\circ\text{C}$ and 700°C . The influence of P_{O_2} on T_C ($\text{N}_2/50$ ppm O_2 or air) is rather low. The valency changes of Mn^{2+} to $\text{Mn}^{3+}/\text{Mn}^{4+}$ and Cr^{3+} to Cr^{4+} both give rise to an increase of T_C at higher T_a and P_{O_2} . For $T_a \leq 700^\circ\text{C}$ and $\text{N}_2/50$ ppm O_2 the T_C shift of Cr^{3+} behaves similar to the ions with a fixed valency, while at higher T_a the increase of T_C indicates the onset of the oxidation to Cr^{4+} . The valence change of Mn^{2+} gradually takes place already at lower annealing temperatures. For annealing in air the data of Cr- and Mn-doped BCTZ reveal a saturation of T_C at high T_a . From these results can be derived that the oxidation of the majority of the incorporated Cr and Mn ions only can be reached at $T_a > 800^\circ\text{C}$ and high oxygen pressure. The material doped with 1 at.% Mn and 0.75 at.% W (Mn-W) exhibits in contrast to single Mn-doped BCTZ a very small T_C -shift vs T_a for both atmospheres. The small Curie point shift observed confirms the formation of stable Mn-W complexes which cannot be oxidized at all.

Due to the high Zr content all materials investigated exhibit a diffuse phase transition [9,10]. Such materials are characterized by a broad dielectric maximum as a function of temperature and a negative value $(T_C - T_0)$, where T_0 denotes the Curie temperature. With increasing acceptor concentration

the diffuse character of the phase transition is enhanced. Also, increasing ionic radius of the acceptors enhances the negative value of $(T_C - T_0)$, due to an increased distortion of the lattice. Figure 4 represents $(T_C - T_0)$ of $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{-}[\text{Ti}_{0.82-x}\text{Zr}_{0.18}\text{A}_x]_2\text{O}_{3-\delta}$ for a constant concentration $x = 0.0075$ of various acceptors A in the reduced state (solid line, solid symbols) and the oxidized state (dashed line, open symbols). The diffuse character is even stronger for divalent acceptors (Mg^{2+}) as compared to trivalent acceptors with comparable ionic radius. It should be noted that the diffuse character of the phase transition is intensified by oxidation.

3.1.2. Donor/Acceptor Complexes. In the case of mixed donor/acceptor doped BCTZ parts of the acceptors are compensated by donors, due to formation of donor-acceptor ‘‘complexes’’. The term complex implies the presence of an average electronically compensated donor-acceptor unit with varying donor-acceptor distance, corresponding to the statistical distribution of the ions at high temperatures. Such materials require less amounts of V_0^{**} for charge compensation of the acceptors. Although Nb donors usually give rise to a strong depression of T_C in BaTiO_3 [11], the increase of the Nb concentration leads to an increase of T_C in reductively fired Nb-Mn doped BCTZ. In complex Mn-Nb and Mn-W doped

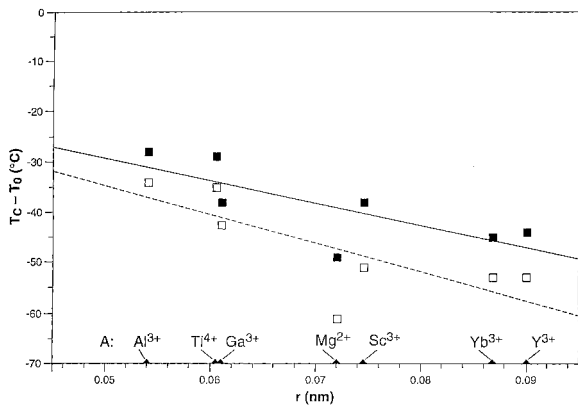
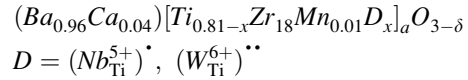


Fig. 4. Difference of the Curie point and the Curie temperature as a function of the ionic radius for different acceptor doped materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{-}[\text{Ti}_{0.8125}\text{Zr}_{0.18}\text{A}_{0.0075}]_{0.995}\text{O}_{3-\delta}$ in the reduced ($\text{Po}_2 = 2 \cdot 10^{-5}$ Pa) and oxidized ($\text{Po}_2 = 5$ Pa) state, represented by the solid symbols (solid line) and open symbols (dashed line), respectively.

materials elimination of V_0^{**} obviously gives rise to the observed increase of T_C . The positive effect of V_0^{**} elimination on T_C thus over-compensates the depressive effect of Nb and W donors on B sites.

Figure 5 demonstrates increasing Curie points for increasing donor concentration x in reduced BCTZ and decreasing Curie points in oxidized ($\text{Po}_2 = 2 \cdot 10^4$ Pa) BCTZ of composition



The difference in Curie point between reduced and oxidized BCTZ becomes smaller and smaller with increasing donor concentration x . At a Nb concentration of $x \simeq 0.01$ and a W^{6+} concentration of $x \simeq 0.05$ the Curie points of reduced and reoxidized material have widely approached each other, i.e., $\delta T_C \simeq 0$. From this can be deduced that for given atomic ratios $\text{Mn}/\text{Nb} = 1 : 1$ and $\text{Mn}/\text{W} = 2 : 1$ the charges of donors and acceptors are compensating each other. Thus, in the case of Mn/Nb doped material the charge complex $[\text{Mn}'\text{-Nb}^{\bullet}]^0$ and for Mn/W $[2\text{Mn}'\text{-W}^{\bullet\bullet}]^0$ are formed. These complexes are stable in reductive ($\simeq 10^{-6}$ Pa) as well as in oxidizing atmosphere ($2 \cdot 10^4$ Pa). From Fig. 5 it is apparent that the oxidation of Mn applies primarily to the Mn which is not involved in the formation of charge complexes. The crossing points

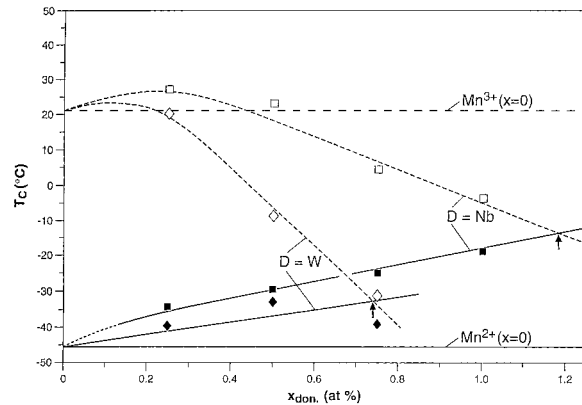


Fig. 5. Variation of the Curie point with increasing donor content for materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{-}[\text{Ti}_{0.81-x}\text{Zr}_{0.18}\text{Mn}_{0.01}\text{D}_x]_{3-\delta}$ with $\text{D} = \text{Nb}, \text{W}$. The results in the reduced ($\text{Po}_2 = 2 \cdot 10^{-5}$ Pa) and oxidized ($\text{Po}_2 = 5$ Pa) state are represented by solid symbols (solid lines) and open symbols (dashed lines), respectively. The lines marked with Mn^{2+} ($x = 0$) and Mn^{3+} ($x = 0$) represent T_C for the corresponding material without donors.

(arrows in Fig. 5) of the T_C curves for the reduced and oxidized state slightly deviate from the expected values, e.g., Mn : Nb = 1 : 1, Mn : W = 2 : 1. This may be attributed to the disordered distribution of donors and acceptors in the material. In the case of Mn/W-doped materials also charge compensation due to the formation of $[\text{Mn}''\text{-W}''']^0$ also might occur. The high stability of these charge complexes is confirmed by the negligible T_C change of Mn/W-doped material with $x=0.0075$ on annealing in oxidizing atmospheres at various temperatures T_a , see Fig. 3.

3.2. Dielectric Constants

The dielectric constant ε and losses $\tan \delta$ of BCTZ ceramics are not only determined by the composition but also to a considerable extent by the processing conditions. In particular the atmosphere during sintering and annealing has a large influence on ε and $\tan \delta$, as can be seen in Figs. 6(a)–6(d) for ceramics of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{-}[\text{Ti}_{0.815}\text{Zr}_{0.18}\text{A}_{0.005}]_{0.995}\text{O}_{3-\delta}$, A = Cr, Mn, Mg, Sc. Any change of the oxygen vacancy and acceptor concentration strongly affects the dielectric properties which are closely correlated with the mobility of ferroelectric domain walls [12].

During re-oxidation of BCTZ doped with valence instable acceptors part of the oxygen vacancies are eliminated. Figure 6(a) and 6(b) shows the temperature dependence of ε and $\tan \delta$ of BCTZ containing 1 mol% Mn or Cr respectively. The solid lines represent the results obtained after sintering in reductive atmosphere and the dashed and dotted lines those obtained after annealing in oxidizing atmosphere ($T_a=1000^\circ\text{C}$, $t_a=2\text{ h}$) with $\text{Po}_2=5\text{ Pa}$ and $\text{Po}_2=2\cdot 10^4\text{ Pa}$ (air), respectively. After re-oxidation ε_{max} is considerably increased and the dielectric losses are strongly decreased in the paraelectric region. Figure 6(e) clearly shows a slight frequency dependence of ε but a large change of $\tan \delta$ for the oxidized Sc-doped material. Similar effects are usually observed in lead containing complex perovskite ceramics which are known as relaxor type dielectrics.

The change of ε and $\tan \delta$ from the reduced to the oxidized state turned out to be a reversible process. This behavior can be attributed to the disappearance of parts of V_0'' at re-oxidation. Acceptor-oxygen vacancy complexes reduce the mobility of ferroelectric domains, thus diminishing ε and $\tan \delta$ in the ferroelectric region (pinning effect) [12]. At the high

temperature end in the paraelectric region large numbers of V_0'' usually give rise to increased ionic conductivity [11,13,14].

However, the change of ε and $\tan \delta$ after re-oxidation also occurs for pure BCTZ, Ca-free compositions and BCTZ doped with valency stable acceptors as demonstrated in Figs. 6(c) and 6(d) for Sc- and Mg-doped BCTZ. The strong increase of ε coincides with the decrease of T_C and appears in the range $500^\circ\text{C} \leq T_a \leq 700^\circ\text{C}$. The insulation resistance also exhibits a strong increase in this range of annealing temperatures and thus strongly suggests an elimination of oxygen vacancies. However, measurable weight changes due to elimination of V_0'' could not be detected with TGA. The change of ε and $\tan \delta$ might be attributed on the one hand to elimination and reorientation [17] of oxygen vacancies, but on the other hand the experimental data suggest the presence of inhomogeneous distributions of oxygen vacancies and complexes, leading to changes of the domain configuration and thus the elastic energy as indicated by different domain pattern before and after annealing, see Fig. 7.

The increase of ε and $\tan \delta$ of Sc- and Mg-doped material is more pronounced than for Mn-doped BCTZ which is due to the much smaller grain size of the Mn-doped ceramics, as outlined in the next section. For the Cr- and Mn-doped ceramics a decrease of ε is observed for lower Po_2 (5 Pa) and $T_a \geq 800^\circ\text{C}$ which corresponds to the elimination of oxygen vacancies due to the oxidation of Cr or Mn at higher T_a . The disappearance of these effects for high Po_2 (in air) suggests the almost complete elimination of oxygen vacancy gradients probably present in the grains at low Po_2 .

3.2.1. Grain Size Effects. The change of the dielectric constant depends on the grain size affecting the stress distribution and the domain configuration in the grain. The grain size dependence of ε has been primarily investigated in ferroelectric materials far below the Curie point [14,15]. Very few has been reported in contrast about the grain size dependence of the dielectric maximum. The variation of ε_{max} with the average grain size, d_{av} , is shown in Fig. 8 for BCTZ of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})\text{-}[\text{Ti}_{0.82-x}\text{Zr}_{0.18}\text{A}_x]_{0.995}\text{O}_{3-\delta}$. The data represent materials, containing various acceptor dopes in concentrations $x \leq 0.01$. Their average grain sizes are compiled in Table 1. The circles

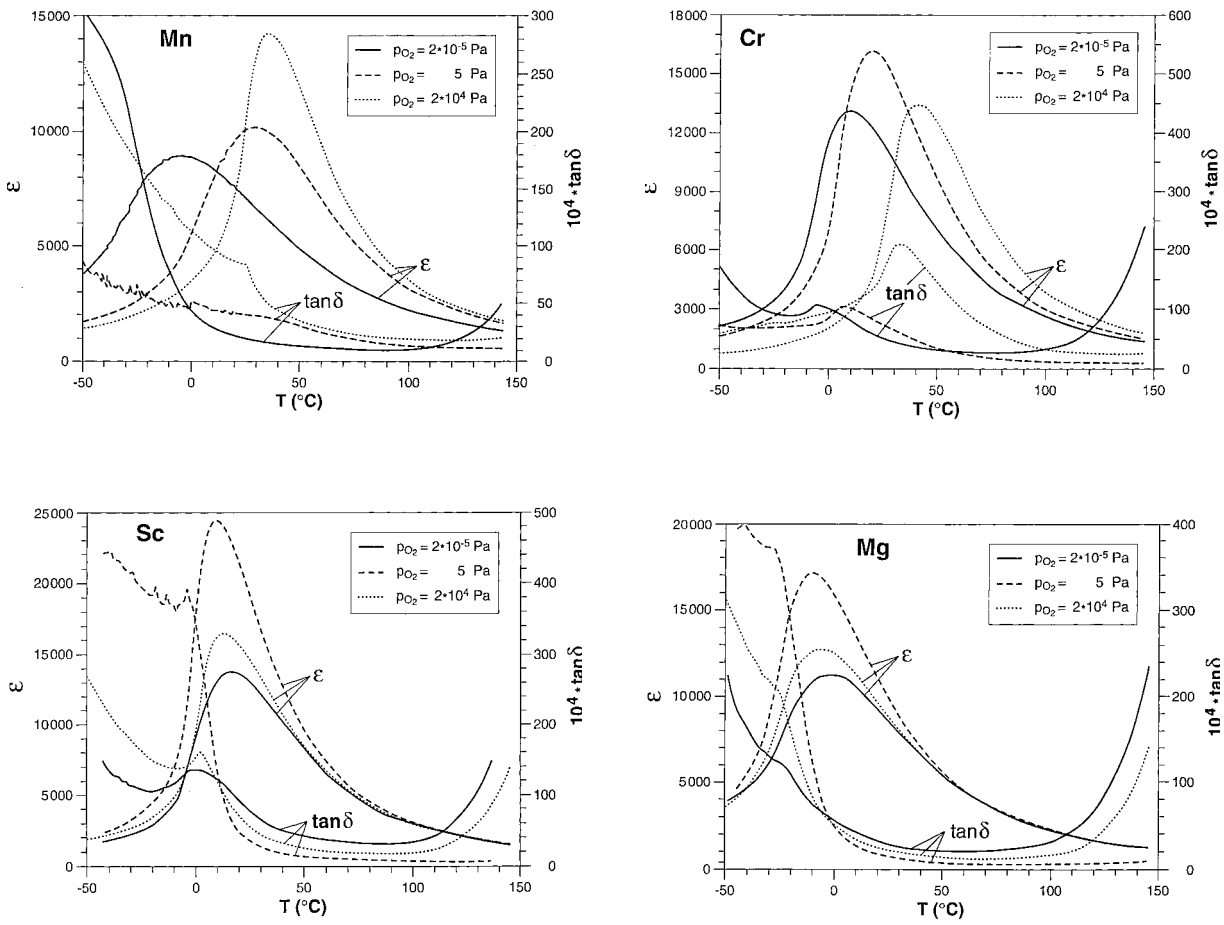


Fig. 6(a-d). Temperature dependence of the dielectric constant ϵ and the dielectric losses $\tan \delta$ for acceptor doped materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})[\text{Ti}_{0.82-x}\text{Zr}_{0.18}\text{A}_x]_{0.995}\text{O}_{3-\delta}$ in the reduced ($P_{O_2} = 2 \cdot 10^{-5}$ Pa: solid line) and oxidized ($P_{O_2} = 5$ Pa: dashed line, $P_{O_2} = 2 \cdot 10^4$ Pa: dotted line) state for (a) A = Mn, (b) A = Cr, (c) A = Sc, (d) A = Mg.

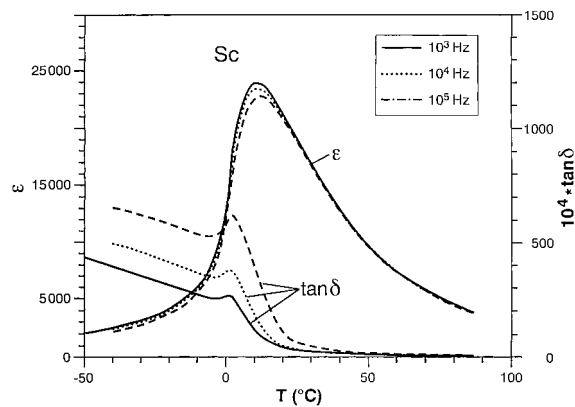
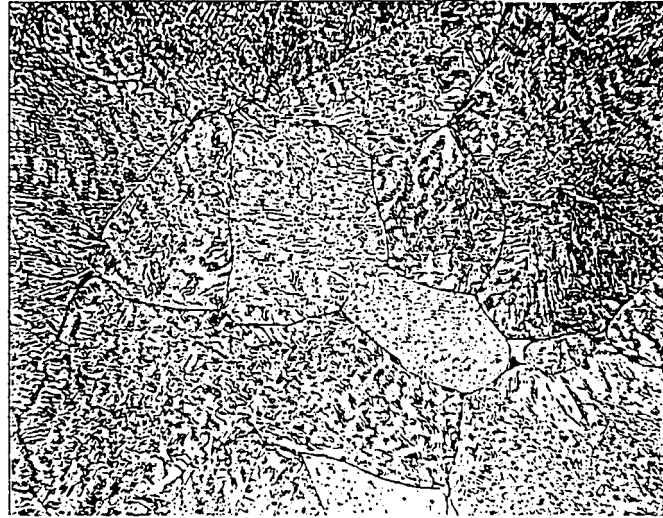
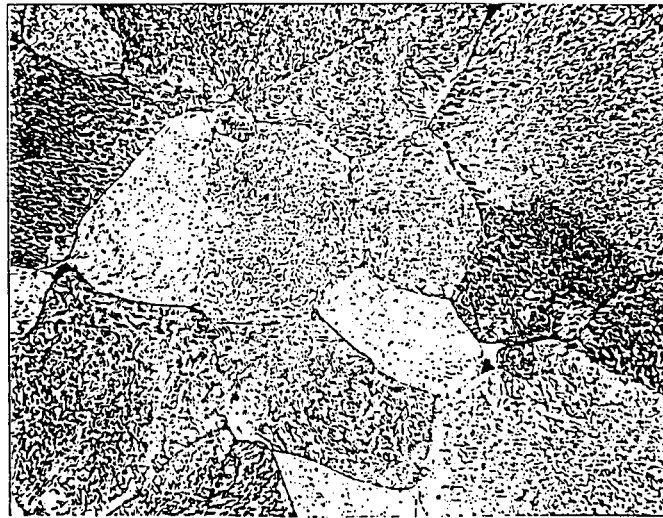


Fig. 6(e). Frequency dependence of the dielectric constant ϵ for oxidized ($P_{O_2} = 5$ Pa) acceptor doped material in the range 1 kHz to 100 kHz: A = Sc.



(a)



(b)

Fig. 7. Domain pattern for an acceptor doped BCTZ ceramic with a Curie point of $\simeq 80^\circ\text{C}$ in the (a) reduced and (b) oxidized state.

represent Mn containing materials. The almost linear relationship between ϵ_{max} and d_{av} is most probably restricted to materials, showing a narrow distribution of grain sizes. The difference of ϵ_{max} between reduced and oxidized materials ($\text{Po}_2 = 5 \text{ Pa}$, 2 h, 1000°C) increases with increasing d_{av} and vanishes almost at grain sizes below $2 \mu\text{m}$. This effect might be attributed to stress induced changes of the domain configuration. These effects are also observed for donor acceptor co-doped compositions [18].

The relatively small scatter of the data suggests that the effect of oxidizing treatment seems to be almost independent of the kind and concentration of particular acceptors. This observation is confirmed by the fact that in BCTZ the maximum dielectric constant is almost the same ($\epsilon_{\text{max}} \simeq 16,000$) at a grain size of $d_{\text{av}} = 4 \mu\text{m}$ for all acceptors studied, see Fig. 9. The data were calculated using the grain size dependence presented in Fig. 8.

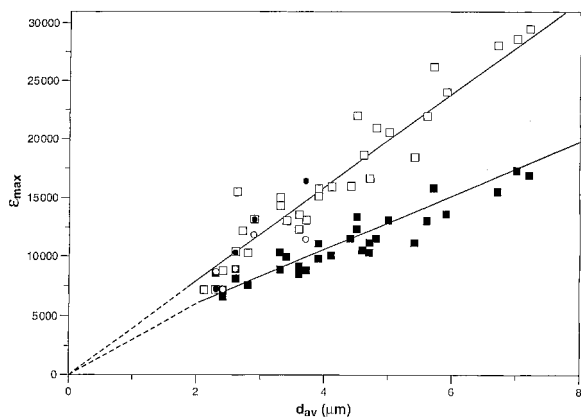


Fig. 8. Maximum dielectric constant as a function of the average grain size for materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})[\text{Ti}_{0.82-x}\text{Zr}_{0.18}\text{A}_x]_{0.995}\text{O}_{3-\delta}$ in the reduced (solid symbols) and the oxidized (open symbols) state for various acceptors and $x \leq 0.01$. Circular symbols: Mn, square symbols: other acceptors.

4. Conclusion

The investigation of acceptor doped BCTZ has shown that the dielectric and ferroelectric properties are influenced in particular by the oxygen vacancies formed for compensation of the acceptors. Charged oxygen vacancies, $V_0^{\bullet\bullet}$, in combination with acceptors obviously give rise to local deformation of the perovskite unit cells, leading to local reduction of

the tetragonal c/a ratio and decrease of the Curie point T_C . The oxygen vacancies can be eliminated by combining acceptors with donors. Elimination of $V_0^{\bullet\bullet}$ by donor-acceptor complexes thus stabilizes the ferroelectric properties, leading to an increase of T_C . The maximum dielectric constant reveals an almost linear increase with the average grain size. The slope depends on the Zr content and annealing conditions.

Reoxidation of acceptor doped BCTZ which has been fired before in reductive atmosphere leads to an increase of permittivity in the ferroelectric region. The effect is also pronounced in materials containing valence stable acceptors, e.g., Mg, Sc. Although in this case the number of oxygen vacancies cannot be decreased by annealing in oxidizing atmosphere, the dielectric effects suggest a reduction of the number of $V_0^{\bullet\bullet}$. Possibly, part of the $V_0^{\bullet\bullet}$ -acceptor complexes pinning the ferroelectric domain walls are reorientated during re-oxidation so that the elastic energy is changed and the mobility of the domains increases.

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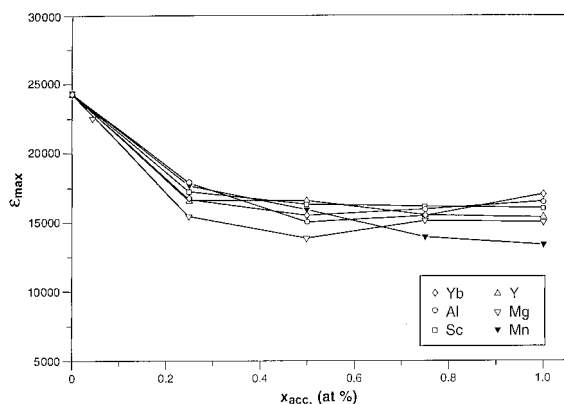


Fig. 9. Concentration dependence of the maximum dielectric constant for materials of composition $(\text{Ba}_{0.96}\text{Ca}_{0.04})[\text{Ti}_{0.82-x}\text{Zr}_{0.18}\text{A}_x]_{0.995}\text{O}_{3-\delta}$ doped with various acceptors A and $x \leq 0.01$. The measured data were corrected to an average grain size of $4 \mu\text{m}$, using the grain size dependence, presented in Fig. 8.

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