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Ca-acceptors in Dielectric Ceramics Sintered in Reducive Atmospheres

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Abstract

Dielectric ceramics of the system $(Ba,Ca)(Ti,Zr)O_3$ *(BCTZ) have been fired with BaO-excess in reducive atmosphere. By the influence of BaO-excess the* Ca^{2+}*-ions are shifted from the Ba- to the Ti-sites of the perovskite lattice. The solubility of* Ca^{2+} *on Ti-sites is largely independent of the firing atmosphere, but shows a pronounced temperature dependence. At 1400°C ≅ 2 at.% Ca can be dissolved on the Ti-sites. Ca-ions on Ti-sites are strong electron acceptors. Highly insulating materials can be thus prepared in reducive atmospheres. The Ca-acceptors are electrically compensated by large numbers of ionized oxygen vacancies. Electromigration of the oxygen vacancies gives rise to ionic conductivity, resulting in low life stability of multilayer capacitors, sintered in reducive atmosphere.*

1 Introduction

Up to now most of the dielectric materials used in ceramic multilayer capacitors (MLCs) are based on barium titanate. For a long time the dielectric ceramics have been cofired with inner electrodes of expensive palladium or palladium silver alloys. After decades of research and development[1,2] the manufacturers of MLCs are now capable of replacing the expensive noble metals by cheaper base metals, e.g. Fe, Co, Ni. Base metal electrodes (BME), however, have to be fired in a protective atmosphere of N_2/H_2 or CO/CO_2. In reducing atmosphere the $BaTiO_3$ forms large numbers of ionized oxygen vacancies,[2] $V(o)^{\bullet\bullet}$. Large numbers of conduction electrons then give rise to high electronic conductivity of the dielectric material, according to the reaction

$$V(o)^x \rightarrow V(o)^{\bullet\bullet} + 2e.$$

The semiconductance of reducive sintered $BaTiO_3$ ceramics can be, however, very effectively suppressed by addition of acceptor dopes. Classical acceptor dopes[1] for $BaTiO_3$ are the ions of Al, Cr, Mn, and Fe. These ions enter the B-sites (Ti-sites) of the perovskite lattice, forming there acceptor-type point defects, like $[Mn^{2+}{}_{(Ti)}]''$, $[Fe^{3+}(Ti)]'$ which strongly trap the conduction electrons.[3] Highly insulating dielectric materials can be thus prepared in reducing atmosphere. BME capacitors, made from acceptor doped $BaTiO_3$ dielectrics exhibit very high insulation resistances (IR) of $\geq 10^{12}\Omega$.[4]

One of the principal problems of transition metal acceptors is the valence instability of transition metal ions, e.g. Cr^{3-}, Mn^{2+}, Fe^{3+}, at a change of the oxygen partial pressure during heat treatment of the MLCs. For this reason manufacturers of BME–MLCs make use of calcium ions on Ti-sites, $[Ca^{2+}{}_{(Ti)}]''$, which have been reported as being very strong acceptors.[5,6] Chan *et al.*[7] found that Ca^{2+}-ions which are well known as A-site substituents may also enter the B-sites of $BaTiO_3$. In the case of BaO-excess a certain number of the Ca^{2+}-ions is shifted from the Ba- to the Ti-sites. Zhuang *et al.*[8] studied the effect of Ca-acceptors on the conductivity and dielectric properties of $BaTiO_3$. They observed a decrease of the tetragonal distortion (c/a) of the perovskite unit cell and a lowering of the Curie point, T_C, at the incorporation of $[Ca^{2+}{}_{(Ti)}]''$ in $BaTiO_3$. Zhang *et al.*[9] reported a maximum solubility of ≅ 5% $[Ca^{2+}{}_{(Ti)}]''$ in $BaTiO_3$.

High-permittivity dielectrics of the temperature specification Y5V are usually prepared from ceramic mixed crystals of the system $(Ba_{1-x}Ca_x)[Ti_{1-y}Zr_y]O_3$ (BCTZ). In BCTZ the Ca^{2+}-ions strongly prefer the Ba-sites of the perovskite lattice,[10] too. At 1300°C a maximum solubility of ≅ 20% $[Ca^{2+}{}_{(A)}]$ was found in $BaTiO_3$.[11] Incorporation of Ca^{2+} on the A-sites yields only slight changes of the lattice parameters and Curie point of $BaTiO_3$.

1.1 Aim of the investigation

The solubility of Ca on the Ti-sites of BCTZ is not yet known. Changes of the Curie point and the unit cell volume will be therefore studied as function of the concentration of $[Ca_{(Ti)}]''$ in BCTZ. Subject of investigation are further the temperature dependence of the solubility of $[Ca_{(Ti)}]''$ and a possible change of the Ca^{2+}-ions from the B-sites back to the A-sites, $Ca_{(Ti)} \rightarrow Ca_{(Ba)}$, in CO_2 or oxidizing atmosphere. The insulation resistance and life stability of reducively sintered BCTZ is studied, using accelerated life tests (ALT).

2 Experimental

2.1 Preparation of BCTZ

The standard experimental material was BCTZ of the composition $(Ba_{0·95}Ca_{0·05})[Ti_{0·88}Zr_{0·12}]O_3$. The atomic ratio of A-site (Ba, Ca) and B-site ions (Ti, Zr) was carefully fixed by analytical means (XFA) at A/B = 1 ± 0·0015. For this the raw materials TiO_2 ('TM1', Fuji Titanium Industries, Ltd, Osaka, Japan) and ZrO_2 ('EF-ULTRA', Z-Tech, Bad Homburg, Germany) had to be analysed for impurities, using ICP analyses and heated for 1 h at 1000°C in O_2 to remove slight oxygen deficits and traces of water. $BaCO_3$ and $CaCO_3$ (both analytical grade, Merck Darmstadt, Germany) were heated for 1 h in a CO_2 stream at 500°C. The small Sr-content of ≅ 0·2 wt% of the $BaCO_3$ was also considered at weighing in. The raw materials were mixed in isopropanole, using an agate ball mill and then calcined to perovskite at 1200°C (6 h) in air.

2.2 Sintering of ceramics

The atomic ratio A/B of the BCTZ was systematically varied by addition of appropriate amounts of TiO_2 or $BaCO_3$ in the range 0·005 mol TiO_2 to 0·15 mol $BaCO_3$. TiO_2 and $BaCO_3$ additives were finely distributed over prereacted BCTZ by wet milling in isopropanole, using 2 mm∅ ZrO_2 balls. Because of the poor sintering behaviour at A/B > 1 the powders must be intensively milled to $d_{50} \cong 0·4$ μm. The powders were uniaxially pressed at 3 kbar to discs of 6 mm diameter and 600 μm thickness. The predensified samples were fired for 2 h at 1400°C in a reducing atmosphere of moist (H_2O-20°C) N_2H_2-95/5. Theoretical densities were determined, using the lattice constants of sintered ceramics. Relative densities of 96–99% of the theoretical value were observed. The highest densities (≥99%) were found at the atomic ratio A/B ≅ 1. With increasing $BaCO_3$ additions the densities decreased. After sintering the diameter of the discs was ≅ 5 mm and the thickness ≅ 500 μm.

2.3 XRD experiments

The lattice parameters of BCTZ ceramics were determined by means of X-ray diffraction (XRD), using Cu–K_α radiation. Due to the large size difference between Ca^{2+}- and Ti^{4+}-ions, strong changes of the lattice parameters are expected to occur at the incorporation of Ca^{2+} on the B-sites. The solubility of Ca on the B-sites was thus determined from the change of the unit cell volume in dependence of the molar amount of added $BaCO_3$.

2.4 Electrical measurements

For electrical measurements 500 μm thick ceramic discs were evaporated with CrNi–Au electrodes. The temperature dependence of the relative dielectric constant *K* was studied in the range -50°C to +150°C, using an automatic capacitance bridge (HP 4278 A). Similar to the lattice parameters also the Curie point T_C of BCTZ is assumed to change with the number of Ca-ions on B-sites. Hence, the solubility of $[Ca^{2+}{}_{(Ti)}]''$ was also determined from T_C changes as function of the BaO-excess in BCTZ.

The life stability of dielectric materials is commonly evaluated from long time measurements of the insulation resistance (IR) under electric field and temperature stress. The long time measurements were abbreviated by employing so-called accelerated life tests (ALT) under specially high temperature stress. The IR of such tested ceramics then breaks down after rather a short time. ALT experiments on BCTZ discs were performed at 250 V and 200°C.

2.5 Thermogravimetric (TGA) experiments

The incorporation of Ca on the B-sites of BCTZ was thermogravimetrically studied on powders, containing various additions of $BaCO_3$. $BaCO_3$-excess pushes the Ca^{2+}-ions from the A- to the B-sites, according to the reaction:

$$(Ba_{1-x}Ca_x)[Ti_{1-y}Zr_y]O_3 + z\,BaCO_3 \qquad (1)$$

$$\rightleftharpoons$$

$$(Ba_{(1+z-x)}Ca_{(x-\frac{z}{2})})\,[Ti_{(1-y)}Zr_yCa_{\frac{z}{2}}]O_{3+z} + z\,CO_2$$

From eqn (1) it can be derived that for each Ca on B-sites two extra Ba-ions have to be incorporated on the A-sites. Thus, formation of *z*/2 $[Ca_{(Ti)}]$ corresponds to the addition of *z* $BaCO_3$. The weight loss due to evaporation of *z* CO_2 at the incorporation of *z* $BaCO_3$ was determined by means of TGA. One of the important questions to be answered by TGA were the extent and the reversibility of reaction (1) in different atmospheres.

According to reaction (1) the total number of perovskite unit cells increases by *z*/2 new units at the addition of *z* BaO to BCTZ. For *z*/2 new perovskite units a corresponding number of 3/2*z* oxygen ions would be necessary to fill up the oxygen sublattice. However, only a number of *z* O^{2-} is available at the incorporation of z BaO. Hence, at the incorporation of z BaO a corresponding number of $z/2$ oxygen vacancies (V(o)) is generated. For each Ca^{2+} on B-sites therefore one oxygen vacancy is formed. In $BaTiO_3$ the Ca-acceptors are compensated by doubly ionized[3] oxygen vacancies.

$$[Ca^{2+}{}_{(B)}]'' \cong [V_{(o)}]^{\bullet\bullet} \cong z/2$$

The actual composition of BCTZ, containing Ca on A- and B-sites and oxygen vacancies is:

$$(Ba_{(A)1-x}Ca_{(A)x})[Ti_{(B)1-y-z}Zr_{(B)y}Ca_{(B)}{}''_{z}]O_{3-z}V_{(o)}{}^{\bullet\bullet}{}_{z} \quad (2)$$

After saturation of the B-sublattice with $[Ca^{2+}(B)]''$ an orthotitanate 2nd phase, similar to Ba_2TiO_4, is most probably formed on further addition of δ $BaCO_3$. The formation of orthotitanate is assumed to be analogous to the known reaction in $BaTiO_3$:

$$BaTiO_3 + \delta\, BaCO_3 \Leftrightarrow \delta\, Ba_2TiO_4 + (1\text{-}\delta)\, BaTiO_3 - \delta\, CO_2 \quad (3)$$

In BCTZ most probably a mixed crystal of $(Ba,Ca)_2TiO_4$ is formed.

For TGA experiments mixtures of BCTZ and z mol $BaCO_3$ in the range $z = 0{\cdot}01$ to $z = 0{\cdot}15$ were prepared. The powder mixtures were prereacted for 2 h at 1400°C in moist (H_2O-20°C) N_2/H_2-95/5. In the thermobalance the crushed powders were several times heated to 1250°C and cooled down to room temperature in streaming CO_2 ($\cong$ 1 bar). The weight changes due to uptake or loss of CO_2 were thus repeatedly measured.

3 Results

3.1 Unit cell volume

Corresponding to the expected shift of Ca^{2+} from A- to B-sites the unit cell volume strongly increased at the incorporation of BaO in BCTZ, see Fig. 1. Up to $BaCO_3$ additions of $z = 0{\cdot}05$ the volume of the perovskite unit cell almost linearly increased (Végards law). The volume increase did not directly start at $z = 0$, but at $z \cong 0{\cdot}005$, indicating a small impurity excess of $\cong$ 0·5% on the B-sites of BCTZ which had to be balanced by the corresponding amount of $\cong$ 0·5% $BaCO_3$. The slight B-excess most probably results from the wear of ZrO_2 milling balls. By interpolation of the Végard lines a maximum solubility of $z = 0{\cdot}045$ BaO in BCTZ was derived.

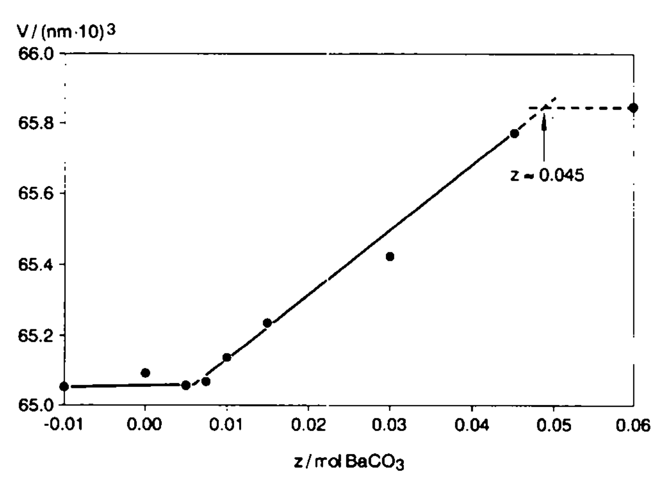

Fig. 1. Change of the unit cell volume of $Ba_{0{\cdot}95}Ca_{0{\cdot}05}(Ca_{0{\cdot}88}Ti_{0{\cdot}12})O_3$ (BCTZ) at the addition of z mol $BaCO_3$ to 1 mol BCTZ; 1400°C, moist (H_2O-20°C) N_2/H_2-95/5.

The XRD diagram of BCTZ fired with $z = 0{\cdot}06$ mol $BaCO_3$ exhibited weak reflexions of a 2nd phase which were almost identical to those of $BaCaTiO_4$.[12] Thus, at $z = 0{\cdot}06$ orthotitanate is formed, analogous to reaction (3). The BCTZ is most probably saturated with BaO already at $z < 0{\cdot}06$. From the value of $z = 0{\cdot}045$ the slight B-excess due to $\cong$ 0·005 mol ZrO_2 wear has to be subtracted. Thus, a maximum solubility of $z \cong 0{\cdot}040$ mol BaO in BCTZ results at 1400°C.

According to eqn (1), the maximum solubility of Ca^{2+} on the B-sites of BCTZ is $z/2 \cong 2$ at.% at 1400°C. This value is considerably lower than the $\cong$ 5 at.% $[Ca^{2+}{}_{(B)}]''$ reported for pure $BaTiO_3$ by Zhang *et al.*[9] In samples containing 0·5% TiO_2-excess, the maximum solubility of Ca^{2+} on the A-sites of BCTZ was found to lie at $[Ca^{2+}{}_{(A)}] \cong$ 16% at 1400°C, see Fig. 2.

3.2 Curie point changes

Similar to the observed changes of the unit cell volume the Curie point T_C is also strongly shifted towards lower temperatures by the incorporation of BaO, see Fig. 3. Due to the slight ZrO_2 wear, the T_C shift starts at $z \cong 0{\cdot}005$ again. The T_C of BCTZ is almost linearly decreasing from +75°C at $z = 0$ to −35°C at $z = 0{\cdot}045$. From this a maximum

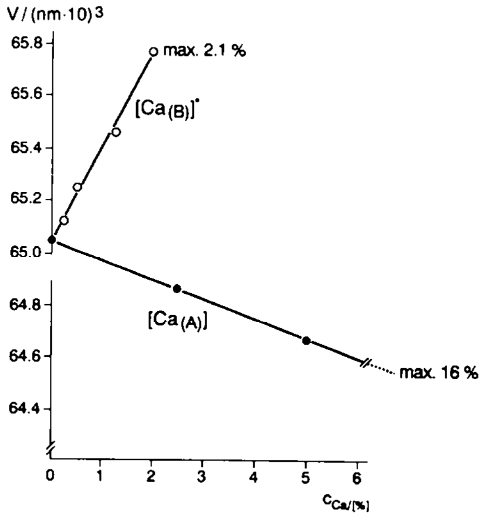

Fig. 2. Change of the unit cell volume of $Ba_{0{\cdot}95}Ca_{0{\cdot}05}(Ca_{0{\cdot}88}Ti_{0{\cdot}12})O_3$ as function of the Ca concentration on A- and B-sites of the perovskite lattice (1400°C).

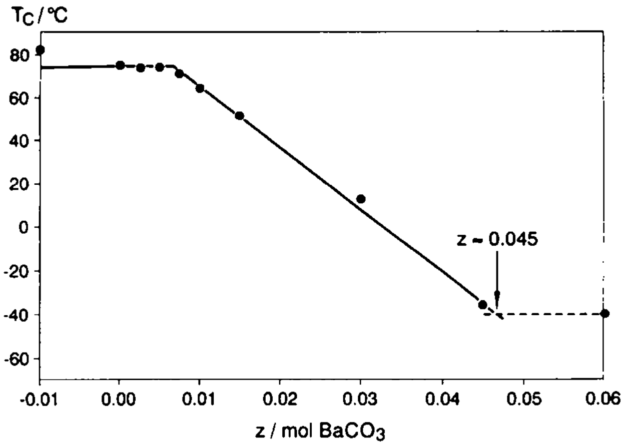

Fig. 3. Curie point shift of $Ba_{0\cdot95}Ca_{0\cdot05}(Ca_{0\cdot88}Ti_{0\cdot12})O_3$ at the addition of z mol $BaCO_3$ to 1 mol BCTZ; 1400°C, moist (H_2O-20°C) N_2/H_2-95/5.

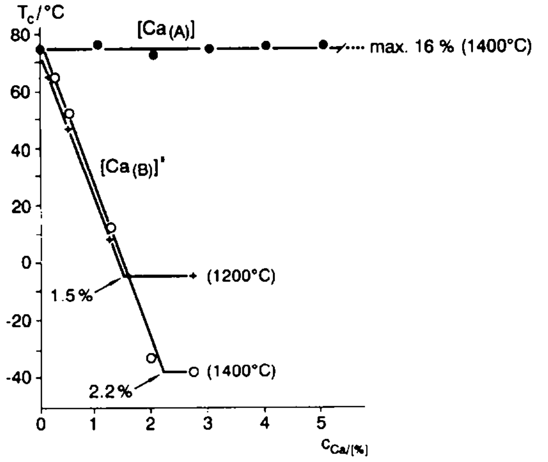

Fig. 4. Curie point shift of $Ba_{0\cdot95}Ca_{0\cdot05}(Ca_{0\cdot88}Ti_{0\cdot12})O_3$ as function of the Ca concentration on A- and B-sites of the perovskite lattice; 1200°C and 1400°C.

solubility of ≅ 2% [Ca^{2-}(B)]" at 1400°C was again evaluated, see Fig. 4. The maximum solubility of [Ca^{2+}(B)]" decreased to ≅ 1·5% after annealing the samples for 2 h at 1200°C. Firing of the samples at various partial pressures of oxygen, (N_2/H_2-95/5 to -99·9/0·1, air and pure O_2) had no measurable influence on T_C. Incorporation of Ca^{2+} on the A-sites of BCTZ had in accordance to the known phase diagrams[10] negligible influence on T_C, see Fig. 4.

3.3 TGA results

The TGA experiments were carried out with prereacted mixtures of BCTZ and $BaCO_3$ in pure CO_2 at 1250°C. At a partial pressure of 1 bar CO_2 the orthotitanate phase Ba_2TiO_4 begins to decompose into $BaCO_3$ and $BaTiO_3$ at temperatures of $T \leq 1135$°C.[13] The decomposition of $(Ba,Ca)_2TiO_4$ into $BaCO_3$, $CaCO_3$ and $(Ba,Ca)TiO_3$ is expected to occur at comparable temperatures.

The TGA experiments revealed negligible weight changes for a BaO excess of $z \leq 0{\cdot}03$, see Fig. 5. At larger BaO-excess ($z > 0{\cdot}03$) a reversible uptake and loss of CO_2 was observed at *ca* 1050°C due to formation of orthotitanate. The lower equilibrium temperature of 1050°C, compared to 1135°C of pure Ba_2TiO_4, suggests a modification of Ba-orthotitanate by dissolved Ca and Zr. With increasing BaO-excess in BCTZ, the weight changes due to uptake and loss of CO_2 also become larger and larger, see Fig. 5. The TGA experiments revealed an irreversible incorporation of Ca^{2+}-ions on the B-sites of BCTZ for $z \leq 0{\cdot}03$, even in CO_2 at $T \leq$ 1250°C. The (Ba,Ca)-orthotitanate phase formed at larger $BaCO_3$ additives, $z > 0{\cdot}03$, is obviously in equilibrium with $(Ba,Ca)CO_3$ and BCTZ at $T \cong$ 1050°C and $p(CO_2) \cong 1$ bar.

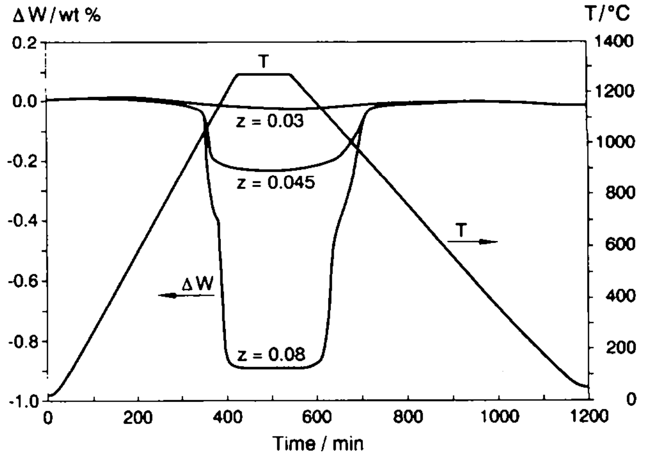

Fig. 5. TGA of $Ba_{0\cdot95}Ca_{0\cdot05}(Ca_{0\cdot88}Ti_{0\cdot12})O_3$ at the addition of z = 0·03, z = 0·045, and z = 0·08 mol $BaCO_3$; 20–1250°C, CO_2 atmosphere.

The reversible weight change Δw, due to the uptake or loss of CO_2 in BCTZ + z $BaCO_3$ at 1250°C was plotted as function of z, see Fig. 6. Most of the measured values of Δw lie on a straight line which becomes $\Delta w = 0$ at $z = 0{\cdot}035$. Considering a ZrO_2 wear of ≅ 0·5%, a maximum solubility of z = 0·03 mol BaO of ≅ 1·5% Ca^{2+} on the B-sites of BCTZ was derived for 1250°C. The

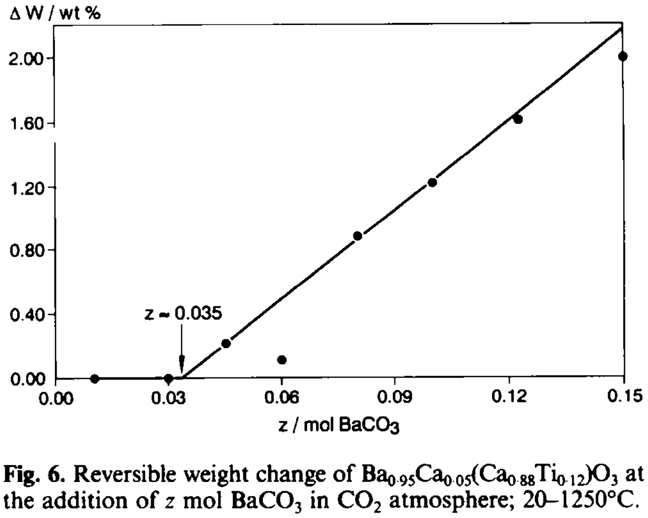

Fig. 6. Reversible weight change of $Ba_{0\cdot95}Ca_{0\cdot05}(Ca_{0\cdot88}Ti_{0\cdot12})O_3$ at the addition of z mol $BaCO_3$ in CO_2 atmosphere; 20–1250°C.

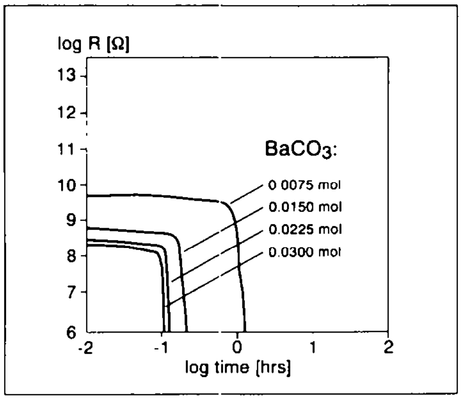

Fig. 7. Life stability at 200°C, 0·5V/,μm of $Ba_{0·95}Ca_{0·05}(Ca_{0·88}Ti_{0·12})O_3$ containing various $BaCO_3$ additives, fired at 1400°C in moist (H_2O-20°C) N_2H_2-95/5.

lower solubility of [Ca(B)]" determined at 1250°C confirms the temperature dependence of the solubility of $[Ca^{2+}{}_{(B)}]$, already detected by means of T_C measurements.

3.4 Insulation resistance (IR) and life stability

Accelerated life tests (ALT) have been performed on ceramic discs at 200°C and 0·5V/μm, see Fig. 7. The discs have been sintered at 1400°C with various $BaCO_3$ additives of $z = 0·0075$ to $z = 0·03$ in moist (H_2O-20°C) N_2/H_2-95/5 atmosphere. The insulation resistance of such treated samples show rather high values of IR = 10^8 Ω to 10^{10} Ω at 200°C. The pale yellow colour as well as the high IR indicate the strong electron trapping effect of the Ca-acceptors. Increase of the BaO-excess from $z = 0·0075$ to $z = 0·03$, however, lowers the IR by more than one decade. This effect can be ascribed to the ionic conductivity, caused by electromigration of charged oxygen vacancies,[14] $[V(o)]^{••}$.

Electromigration of ionized oxygen vacancies in dc fields was found to be the major reason for the electrical degradation of $BaTiO_3$-based perovskite dielectrics.[15,16] Charged oxygen vacancies, formed for compensation of the Ca-acceptors are thus assumed to be responsible for the rather poor life stability of BCTZ, fired with BaO-excess. As can be seen in Fig. 7, the life time of BCTZ strongly decreases with increasing amount of BaO-excess, z.

4 Summary and Discussion

The investigation of $(Ba_{0·95}Ca_{0·05})(Ti_{0·88}Zr_{0·12})O_3$ (BCTZ) confirmed earlier results obtained on pure $BaTiO_3$, that Ca^{2+}-ions are shifted from the A- to the B-sites by the influence of BaO-excess. Even at 1400°C the maximum solubility of ≅ 2% $[Ca^{2+}{}_{(B)}]$ in BCTZ is below that reported for pure $BaTiO_3$[9] (5%). The solubility of Ca^{2+}-acceptors on the B-sites of BCTZ shows a distinct temperature dependence, but was found to be independent of the oxygen partial pressure of the firing atmosphere. It has been also confirmed that $[Ca^{2+}{}_{(B)}]''$ is a strong electron-acceptor in BCTZ. Ba-excess ($A/B > 1$) can be thus successfully employed for suppressing the electronic conduction in BCTZ-based dielectric materials cofired with Ni electrodes in reducive atmosphere. While the electronic conductivity of Ca-acceptor doped BCTZ is very low, a large number of charged oxygen vacancies, $[V(o)]^{••}$ gives rise to a considerably high ionic conductivity. The mobility of the ionized oxygen vacancies $[V(o)]^{••}$ in the electrical field is considered as responsible for the rapid degradation of Ca-acceptor doped BCTZ under dc field and temperature stress. Hence, additional dopes are needed to suppress the ionic conduction in BME multilayer capacitors prepared from BCTZ dielectric materials with BaO-excess.

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