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High-Permittivity Dielectric Ceramics with High Endurance

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Abstract

Donor-doped $BaTiO_3$ ceramics show very high endurance under DC field stress and are therefore suitable candidates for the manufacture of multilayer capacitors with thin dielectric layers. CeO_2 additives were found to be excellent donor dopants. The donor effect results from Ce^{3+} ions incorporated on Ba sites of the perovskite lattice. Defect chemistry, solubility of CeO_2 in $BaTiO_3$ and the ferroelectric phase transition of Ce-modified $BaTiO_3$ have been studied by several methods.

Keramiken aus donator-dotiertem Bariumtitanat zeichnen sich durch eine sehr hohe Lebensdauer bei starker Gleichspannungsbelastung aus und sind deshalb zur Herstellung von Vielschichtkondensatoren mit dünnen dielektrischen Schichten besonders gut geeignet. Zusätze aus CeO_2 erwiesen sich als hervorragende Donatordotierungen. Der Donator-Effekt rührt von Ce^{3+}-Ionen her, die auf den Ba-Plätzen des Perowskitgitters eingebaut werden. Defektchemie und Löslichkeit von CeO_2 in $BaTiO_3$, sowie die Thermodynamik der ferroelektrischen Phasenumwandlung von Ce-dotiertem $BaTiO_3$ wurden mit verschiedenen Methoden untersucht.

Les céramiques à base de $BaTiO_3$, dopées en donneurs, ont une résistance très élevée sous champ électrique continu et sont donc de bons candidats pour la fabrication de condensateurs multicouches contenant de fines couches de diélectriques. CeO_2, utilisé comme additif, s'est révélé un excellent dopant en donneurs. Cet effet dopant provient des ions Ce^{3+}, occupant des sites du barium dans le réseau de la perovskite. On a étudié la chimie des défauts, la solubilité de CeO_2 dans $BaTiO_3$ et la transition ferroélectrique de $BaTiO_3$ avec addition de Ce par plusieurs méthodes.

1 Introduction

For a number of simple electronic applications, e.g. noise suppression, decoupling, high- and low-pass filters, ceramic multilayer capacitors (MLCCs) of relatively poor temperature stability are satisfactorily used. The dielectric temperature characteristics of these MLCCs usually meet the Electric Industries Association (EIA) temperature specification 'Y5V'. The specification Y5V allows for capacitance changes of +22% to −82% of the 25°C reading in the temperature range of −30°C to 85°C.

In the area of electronic components a continuous trend of miniaturization is going on in which the multilayer chip capacitors are also participating. The rapidly growing market of surface-mounted technology chips therefore demands MLCCs of higher and higher compactness, i.e. higher capacitance per volume. The required increase of the specific capacitance is realized in two ways:

—Raising of dielectric constants.
—Reduction of the dielectric layer thickness.

Y5V dielectric materials commonly make use of the high permittivity maximum, occurring at the Curie point (T_c) of ferroelectric materials. The temperature characteristics of Y5V materials usually correspond to a simple, broad dielectric maximum close to room temperature. The most often used basic material for MLCCs is ferroelectric $BaTiO_3$, showing a T_c of 130°C. The dielectric maximum is shifted towards room temperature by chemical modification of the ceramic material.

After more than 40 years optimization of $BaTiO_3$ dielectrics (in disc capacitors as well as in MLCCs) the enhancement of the dielectric maximum has obviously come to a certain limit of $\varepsilon_r \cong 16000$ in Y5V materials. This maximum value will therefore be most probably not largely exceeded in the future.

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A novel class of dielectric materials are the 'ferroelectric relaxors'[1] which were found to have much higher permittivities than $BaTiO_3$-based dielectrics of $\varepsilon_r \cong 20\,000$.[2] However, relaxor materials exhibit a number of disadvantageous properties[3] which are a strong frequency dependence and high aging rate of ε_r and $\tan\delta$ ('relaxor' effect) and lower dielectric and mechanical strength[4] than $BaTiO_3$ ceramics. Moreover, most of the relaxor materials are based on PbO-containing complex perovskites, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN).[5] At present, the high permittivity of lead relaxor materials cannot outweigh the mechanical instability and the environmental problems emerging from the toxicity of PbO vapour and dust. The classical $BaTiO_3$-based ceramics therefore still dominate the market of Y5V MLCCs.

Further increase of the specific capacitance of MLCCs seems only possible by a reduction of the dielectric layer thickness. However, with lower thickness of the dielectric layers new problems come up which are, for instance, dielectric breakdown and electrical degradation under DC field stress. As shown by Waser and coworkers,[6] electrical transport of charged oxygen vacancies through the dielectric layer is principally responsible for limitation of the life of MLCCs exposed to high DC field and temperature stress. Due to their lower content of oxygen vacancies, the life stability of donor-doped materials[7] is by several orders of magnitude higher than that of acceptor-doped $BaTiO_3$.

1.1 High *K* Y5V materials

One of the most often used, classical high *K* Y5V materials are mixed crystals of $(Ba,Ca)(Ti,Zr)O_3$. In this system the isovalent substituent Zr^{4+} is not only a simple Curie point shifter, but also gives rise to a gradual change of the ferroelectric phase transition at the Curie point T_c from first to second order.[8] In ceramics of the mixed crystal $Ba(Ti_{1-y}Zr_y)O_3$ the change to second-order transition occurs at about $y \cong 0{\cdot}13$.

The level of the dielectric maximum at T_c of a ferroelectric crystal is given by the Curie–Weiss formula:

$$\varepsilon_{r,max} = C_w/(T_c - T_0)$$

In this formula C_w is called the Curie constant. The Curie–Weiss temperature T_0 is determined by extrapolation of $1/\varepsilon_r(T) \Rightarrow 0$.

In a second-order ferroelectric phase transition both the Curie point T_c and the Curie–Weiss temperature T_0 coincide: $T_c \cong T_0$, i.e. $(T_c - T_0) = 0$. According to the phenomenological theory of ferroelectric phase transitions,[9,10] the Curie peak at T_c of a second-order ferroelectric phase transition should therefore become infinitely high: $\varepsilon_{r,max} \Rightarrow \infty$. In fact, mixed crystals of $Ba(Ti_{1-y}Zr_y)O_3$ exhibit huge dielectric maxima of $\varepsilon_{r,max} \geq 40\,000$ at $y \cong 0{\cdot}13$.[8] These maxima, however, are usually too sharp and do not fit into the temperature specification Y5V.

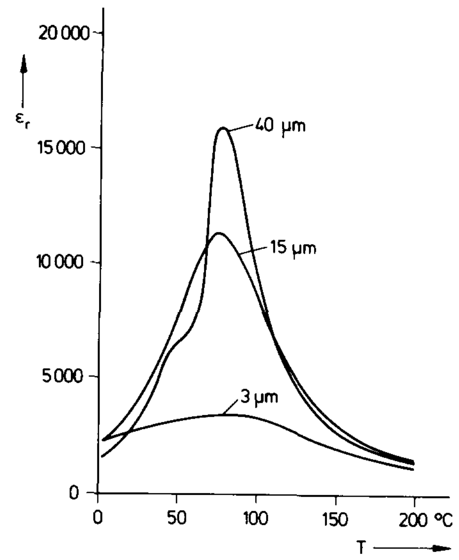


Fig. 1. Grain size dependence of the dielectric Curie maximum in a conventional high-permittivity dielectric material $(Ba_{0{\cdot}87}Ca_{0{\cdot}13})(Ti_{0{\cdot}88}Zr_{0{\cdot}12})O_3$.

The permittivity of ferroelectric $BaTiO_3$ ceramics generally shows a strong dependence on the grain size.[11] Curie peaks of $Ba(Ti_{1-y}Zr_y)O_3$ ceramics are thus very sensitive to any alterations of the grain size. Even moderate reductions of the average grain size give rise to strong broadening and flattening of the dielectric maximum (see Fig. 1). The trend to form diffuse, smeared out Curie maxima is found particularly in ferroelectric ceramics showing a second-order phase transition. Hence, $Ba(Ti_{1-y}Zr_y)O_3$ of $y > 0{\cdot}13$ and $d \leq 3\,\mu m$ average grain size exhibit broad, diffuse Curie maxima of $\varepsilon_{r,max} = <4000$.

1.2 Donor-doped Y5V materials

Donor dopants like La^{3+} on Ba sites or Nb^{5+} on Ti sites are well known for their strong grain growth inhibiting effect in $BaTiO_3$. At donor concentrations of $\geq 0{\cdot}5$ mol% a sudden decrease of the average grain size generally occurs. Even now, this so-called 'grain growth anomaly'[12,13] of donor-doped $BaTiO_3$ has not been a well understood phenomenon. In donor doped $(Ba,Ca)(Ti,Zr)O_3$, the grain growth anomaly leads to an intolerable flattening of the dielectric Curie maximum. Hence, improvement of the life stability of classical $BaTiO_3$-based Y5V materials by the way of donor doping does not seem practicable.

However, there is one exception to the rule: the long-used additive CeO_2[14] is known to shift the Curie point of $BaTiO_3$ to room temperature without

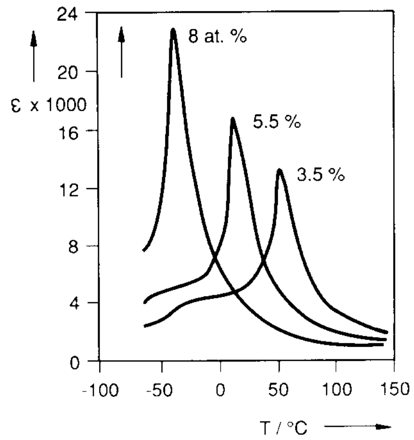


Fig. 2. Dielectric maxima at the Curie point of mixed crystals of $(Ba_{1-x}Ce_x)TiO_3$ (average grain size 2 μm).

flattening the dielectric maximum (see Fig. 2). CeO_2 was recently reported to act as donor dopant in $BaTiO_3$.[15] In addition, the raising of the dielectric maximum, observed at increasing Ce concentration, suggests the alternation of the phase transition from first- to second-order.

1.3 Cerium-doped Y5V materials

The literature about the doping character of Ce in $BaTiO_3$ is rather contradictory. Up to now, there has been little known about valency state, lattice site occupation and solubility of Ce ions in $BaTiO_3$. A study by Kolar *et al.*[16] reports incorporation of Ce^{4+} in $BaTiO_3$ and solubility of *c*. 15–20 mol% $Ba(Ce^{4+})O_3$ in $BaTiO_3$. This result is in contradiction to the work of Itakura *et al.*,[15] who found substitution of Ba^{2+} by Ce^{3+} on the A-sites of the perovskite lattice ABO_3. Regarding the multivalency of cerium ($Ce^{3+} \leftrightarrow Ce^{4+}$), ions of Ce should be able to enter both the Ba sites and the Ti sites. Valency state, lattice site occupation and solubility of Ce in $BaTiO_3$ are central questions to the understanding of the doping character of Ce in $BaTiO_3$-based Y5V dielectrics which should therefore be resolved by doing new experiments.

2 Experimental

2.1 Sample preparation

Ce-doped $BaTiO_3$ was prepared by mixing high purity $BaTiO_3$ ('HPB', TAM, Niagara Falls, USA) with various amounts of CeO_2 (reagent grade, Merck, Darmstadt, Germany) and TiO_2 ('TP13', Fuji Titanium Industry, Tokyo, Japan) in different atomic ratios of $0 \leq Ti/Ce \leq 1{\cdot}5$. The Ba/Ti atomic ratio of the $BaTiO_3$ was determined to 1:1·006, using X-ray fluorescence analyses (XFA, Philips PW 1404). Before mixing the raw materials were milled to extremely fine grain sizes of $\leq 0{\cdot}3$ μm, using wear-resistant Y-stabilized ZrO_2 (Tosoh, distributed by Krahn Chemie GmbH, Hamburg, Germany) balls of 2 mm ϕ. Additional samples were prepared by calcining appropriate amounts of $BaCO_3$ (Selectipur, Merck, Darmstadt, Germany), TiO_2 and CeO_2 at 1100–1200°C in air. The incorporation of CeO_2 was controlled by means of X-ray diffraction (XRD), light and scanning electron microscopy (SEM).

2.2 Sintering experiments

Ceramic discs from 6 mm ϕ and 0·6 mm thickness were mechanically pressed and fired at temperatures of 1200–1400°C in N_2, O_2 and in air. For dielectric measurements the discs were evaporated with thin Cr/Ni–Au layers. The densification was found to be crucially dependent on the molar ratio of Ti/Ce in the additive. For atomic ratios $Ti/Ce < 0{\cdot}7$ sintering results were rather poor, while at ratios of $Ti/Ce > 0{\cdot}7$ highly dense, reddish ceramics were obtained.

2.3 Thermogravimetry (TGA) and dielectric measurements

Dielectric measurements were performed on sintered discs at 1 kHz and 1 V rms in the temperature range of −100 to 150°C, using a multi-frequency LCR meter (Hewlett Packard 4274A). Thermogravimetric measurements were carried out in a thermobalance (TGA/DTA) (Netsch STA-429) in various atmospheres (O_2, air, N_2 (<5 ppm O_2) and N_2/H_2) at temperatures up to 1500°C. The evolution of even small amounts of O_2, corresponding to the change of CeO_2 to Ce_2O_3, could be readily detected in TGA.

3 Results

3.1 TGA: The valency state and defect chemistry of Ce in $BaTiO_3$

Tetravalent ions of cerium are known for their high valence stability. The chemical change of CeO_2 to Ce_2O_3 is thus reported to occur at temperatures above 1250°C[17] in reducing atmosphere, corresponding to the reaction:

$$2CeO_2 \leftrightarrow Ce_2O_3 + \tfrac{1}{2}O_2$$

However, even in pure oxygen atmosphere at 1150°C, the weight losses of $BaTiO_3$ samples containing equimolar additives of 3·5 mol% CeO_2 and TiO_2 practically corresponded to a complete transformation of Ce^{4+} into Ce^{3+} (see Fig. 3). At higher concentrations (>5 mol%) more and more Ce was maintained in the tetravalent state (see Fig. 4). Thus, at 12 mol% Ce only 70% of the Ce adopted the trivalent state. TGA and SEM indicated the importance of the molar ratio of TiO_2/CeO_2 in the

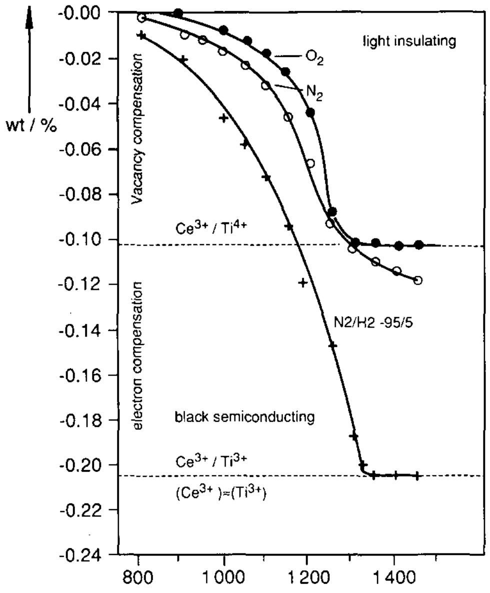


Fig. 3. Oxygen losses due to formation of Ce^{3+} and Ti^{3+} in $BaTiO_3$ fired with additions of 3·5 mol% of (TiO_2/CeO_2–1:1) in various atmospheres.

additive for the incorporation of CeO_2. For molar ratios of $TiO_2/CeO_2 < 0{\cdot}7$ incomplete incorporation of Ce in $BaTiO_3$ was found.

CeO_2-doped $BaTiO_3$ fired in oxidizing atmosphere is electrically highly insulating and of light reddish colour. On firing in purified N_2 (5 ppm O_2), the oxygen losses were slightly higher than expected for complete transformation to Ce^{3+}. In stronger reducing atmospheres, (N_2/H_2—95/5, moistened in H_2O at 20°C) the oxygen loss of $BaTiO_3$ + 3·5 mol% ($CeO_2 + TiO_2$) was exactly twice as high as required for transformation to Ce^{3+} (see Fig. 3). Such fired ceramics turned out to be deeply black coloured semiconductors. From the observation that Ce^{3+} is only formed when TiO_2 is added to $BaTiO_3$ in combination with CeO_2 it is derived that Ce^{3+} ions enter the Ba sites of the perovskite lattice. Ce^{3+} ions are thus typical donors: ($Ce^{\cdot}_{(Ba)}$).

In $BaTiO_3$ the excess charge of donors is compensated either by metal vacancies ('vacancy compensation') or by conduction electrons ('electron compensation').[7] In oxidizing atmosphere (air) the Ce^{3+} donors on Ba sites are obviously compensated by metal vacancies. Vacancy compensation of rare earth ions is a long known phenomenon in $BaTiO_3$,[7] leading to electrically highly insulating ceramics. In reducing atmosphere Ce^{3+}(Ba) is in contrast compensated by equivalent numbers of Ti^{3+} ions. In this case TGA reveals equivalent amounts of Ti^{4+} to be reduced to Ti^{3+}:

$$(Ce^{3+}_{(Ba)}) \cong (Ti^{3+}_{(Ti)})$$

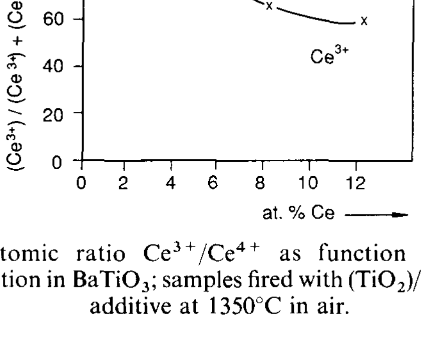


Fig. 4. Atomic ratio Ce^{3+}/Ce^{4+} as function of the Ce concentration in $BaTiO_3$; samples fired with (TiO_2)/CeO_2—1:1) additive at 1350°C in air.

At room temperature Ti^{3+} easily emits conduction electrons, corresponding to:

$$Ti^{3+} \rightarrow Ti^{4+} + e$$

The black samples, formed by electron compensation in reducing atmosphere are excellent semiconductors. It is important to note that Ce^{4+} ions on Ti sites are not easily available for reduction. Only in heavily reducing atmosphere are tetravalent ions on B sites of ABO_3, e.g. Ce^{4+}, Ti^{4+} also partly reduced to the trivalent state. Trivalent ions on B sites are acceptors which were found to be compensated by appreciable numbers of ionized oxygen vacancies:[7]

$$Ce^{4+}_{(Ti)} \underset{\ll p_{O_2}}{\rightarrow} Ce'_{(Ti)} + 1/2V_{(0)}^{\cdot\cdot} + 1/4O_2$$

3.2 Solubility and phase relations of CeO_2/TiO_2 in $BaTiO_3$

The extent of cerium dissolution in $BaTiO_3$ strongly depends on the Ce/Ti atomic ratio of the additive. Dissolution of CeO_2 in the perovskite matrix of $BaTiO_3$ was controlled by SEM analyses and determination of Curie point shifts.

Up to Ce concentrations of 8 mol%, a linear decrease of T_c of 21°C per mol% Ce was found in ceramics fired at 1350°C in air with equimolar additives of TiO_2 and CeO_2. In light microscopy and SEM these ceramics already showed certain small segregations of the Ti-rich second phase $Ba_6Ti_{17}O_{40}$. Samples fired with additives of the atomic ratio $Ti/Ce < 0{\cdot}6$ exhibited partly unreacted CeO_2 and open porosity. Systematic studies of phase relations and T_c shifts in $BaTiO_3$, fired with various amounts of CeO_2 and TiO_2 additive revealed the existence of monophasic perovskite only in a narrow range of TiO_2/CeO_2 ratios of $0{\cdot}6 < Ti/Ce < 1$ (see Fig. 5).

The change from Ce^{4+} to Ce^{3+} obviously takes place at a rather late period of densification of $BaTiO_3$-TiO_2/CeO_2. In this 'final stage' of sintering the ceramic material has already attained a high density. The oxygen evolved during decomposition of CeO_2 therefore cannot rapidly escape from the ceramic material. The big pin holes often found in CeO_2 modified $BaTiO_3$, were probably blown up by

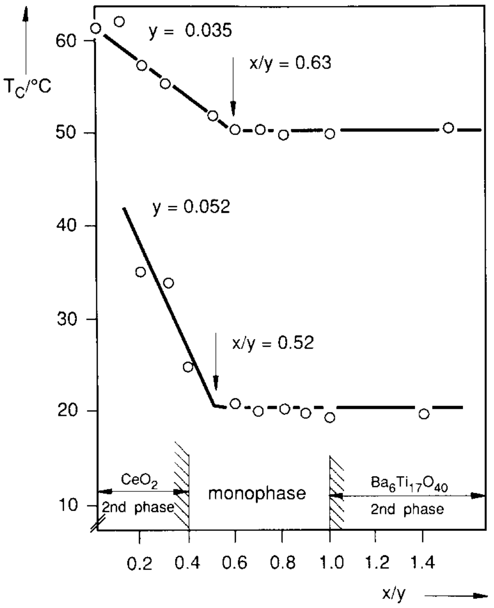


Fig. 5. Monophasic perovskite region of $BaTiO_3$, fired at 1400°C with 3·5 mol% and 5·2 mol% CeO_2 and various co-additives of TiO_2. Phase relations determined by means of T_C shifts and light microscopy.

escaping O_2 (see Fig. 6). The small grain size of $d_{av} \cong 2$–$3\,\mu m$ of $BaTiO_3$–5·2 mol% (CeO_2/TiO_2–1:1), shown in Fig. 6, is quite typical of donor-doped $BaTiO_4$.

3.3 Defect chemical model of Ce-doped $BaTiO_3$

3.3.1 Vacancy compensation

Defect chemical studies of La-doped $SrTiO_3$[18] and $PbTiO_3$[19] in oxidizing atmosphere clearly revealed both the incorporation of $La^{\bullet}$ donors and formation of vacancies on the A sites of the perovskite lattice ABO_3. When $Ce^{\bullet}$ donors on Ba sites are compensated by A site vacancies large amounts of TiO_2 co-additive would be necessary to form monophasic perovskite, corresponding to the reaction:

$$2CeO_2 + 3TiO_2 \rightarrow$$
$$3((Ce^{\bullet}{}_{(Ba)})_{2/3}(V''_{(Ba)})_{1/3}(Ti_{(Ti)})(O_{(O)})_3) + \tfrac{1}{2}O_2$$
$$TiO_2/CeO_2 = 1{\cdot}5$$

The large amounts of TiO_2 co-additive, necessary in accordance to the reaction of A site vacancy compensation of $Ce^{\bullet}$ donors, are in clear contradiction to the experimental facts. Segregation of Ti-rich second phase already takes place at the molar ratio $TiO_2/CeO_2 \cong 1$. The range of molar ratios of $0{\cdot}6 < TiO_2/CeO_2 < 1$ at which monophasic perovskite is observed strongly suggests formation of vacancies on Ti sites, corresponding to the reaction:

$$4CeO_2 + 3TiO_2 \rightarrow$$
$$4((Ce^{\bullet}_{(Ba)})(Ti_{(Ti)})_{3/4}(V''''_{(Ti)})_{1/4}(O_{(O)})_3) + O_2$$
$$TiO_2/CeO_2 = 0{\cdot}75$$

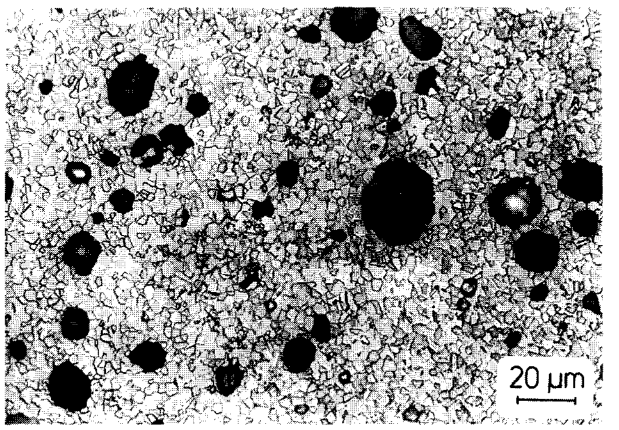


Fig. 6. Pin holes in $BaTiO_3$–CeO_2, blown up by O_2 at the valence change $Ce^{4+} \Rightarrow Ce^{3+}$.

The molar ratio of $TiO_2/CeO_2 = 0{\cdot}75$, required for B site vacancy compensation of $Ce^{\bullet}$ donors, fits the experimental results much better. Formation of Ti site vacancies has been already reported by Jonker & Havinga[20] for La^{3+} donor-doped $BaTiO_3$. Hence, it is quite reasonable that Ce^{3+} ions, having a similar ionic radius to La^{3+}, show the same compensation mechanism.

It should be noted that the molar ratio of $TiO_2/CeO_2 = 0{\cdot}75$, required for the formation of vacancies on Ti sites, is only valid for combinations Ti/Ce^{3+}. Considering the small amounts of Ce^{4+} on Ti sites (Fig. 4), the actual ratio of Ti/Ce of the additive must be $Ti/(Ce^{3+} + Ce^{4+}) < 0{\cdot}75$. The ratios of $TiO_2/CeO_2 = 0{\cdot}65$ and $0{\cdot}55$, experimentally determined for the formation of monophasic perovskite at additions of 3·5 mol% and 5·2 mol% CeO_2 respectively, thus find a plausible explanation.

Considering the amounts of $Ce^{4+}_{(Ti)}$, the defect chemical formula of Ce-doped $BaTiO_3$ is given for oxidizing atmospheres by:

$$[(Ba_{(Ba)})_{1-u}(Ce^{\bullet}_{(Ba)})_u][(Ti_{(Ti)})_{1-(v+(u/4))}$$
$$\times (Ce^{\bullet}_{(Ti)})_v(V''''_{(Ti)})_{u/4}](O_{(O)})_3$$

According to this formula for oxidized samples the total concentration of Ce in $BaTiO_3$ is $y = u + v$. With increasing Ce concentration y, the ratio of u/v, i.e. Ce^{3+}/Ce^{4+}, shifts towards higher values of v (Ce^{4+}). As far as the Ce^{3+} donors on Ba sites are compensated by $u/4$ B site vacancies, the dielectric material is electrically insulating.

3.3.2 Electron compensation

On firing Ce-doped materials in reducing atmospheres (N_2/H_2), electron compensation of the $Ce^{\bullet}$ donors on A sites takes place. For reductive treatment the defect chemical formula is given by:

$$[(Ba_{(Ba)})_{1-u}(Ce^{\bullet}_{(Ba)})_u]$$
$$\times [(Ti_{(Ti)})_{1-u-v}(Ti'_{(Ti)})_u(Ce^{\bullet}_{(Ti)})_v](O_{(O)})_3$$

The number u of Ti acceptors is equivalent to the number of conduction electrons. The difference in conductivity between vacancy- and electron-compensated Ce-doped $BaTiO_3$ amounts to *c.* 13 orders of magnitude.

4 The Ferroelectric Phase Transition of CeO_2-doped $BaTiO_3$

In $BaTiO_3$–CeO_2 the increase of the dielectric peak strongly suggests a gradual change of the phase transition at T_c from first to second order at increasing Ce concentration. The crucial criterion for a second-order phase transition is zero latent heat at T_c: $\Delta H_{(T_c)} = 0$. The latent heats at T_c of sintered $(Ba_{1-x}Ce_x)TiO_3$ and $Ba(Ti_{1-y}Zr_y)O_3$ were therefore determined by means of quantitative DTA (TA 2000, Mettler, Zürich, Switzerland).

As a surprising result of DTA a coincidence of the concentration dependence $Q_L = f(x,y)$ at T_c of $(Ba_{1-x}Ce_x)TiO_3$ and $Ba(Ti_{1-y}Zr_y)O_3$ was found (see Fig. 7). In both materials the latent heats at T_c disappear at a doping concentration of 10 mol% (for both Ce, and Zr). The Curie maxima of both materials should therefore be of comparible sensitivity to alterations of the grain size. $(Ba_{1-x}Ce_x)TiO_3$, however, shows at a grain size of $\cong 3\,\mu m$ and $T_c \cong 50°C$ still $\varepsilon_{r(max)} \cong 12\,000$ (see Fig. 2, $x = 0{\cdot}035$), while ceramics of $(Ba_{0{\cdot}87}Zr_{0{\cdot}13})(Ti_{0{\cdot}88}Zr_{0{\cdot}12})O_3$ exhibit $\varepsilon_{r(max)} \leq 4000$ under comparable conditions (see Fig. 1). The different sensitivity of the Curie peaks to reduction of the grain size, observed in the two materials can be explained in terms of thermodynamic considerations.

5 Thermodynamic Consideration of the Ferroelectric Phase Transition

The free energy change ΔG_{Tr} of the transition from the ferroelectric (FE) to the paraelectric state (PE) at a temperature $T \neq T_c$ is widely determined by the following parameters:

—Temperature T,
—Latent heat $Q_L \cong \Delta H_{Tr}$ (transition entropy $\Delta S_{Tr} \cong Q_L/T_c$),
—Excess energy ΔG^E, interfering with ΔG_{Tr}.

The excess energy ΔG^E results from a slight scatter of the chemical composition and local fluctuations of mechanical stress. The internal stress is caused by the misfit of tetragonally distorted grains in the ferroelectric state at $T \leq T_c$.[21,22] Fluctuations of ΔG^E are assumed to be responsible for the emergence of diffuse ferroelectric phase transitions, showing broad and flat Curie peaks.[8]

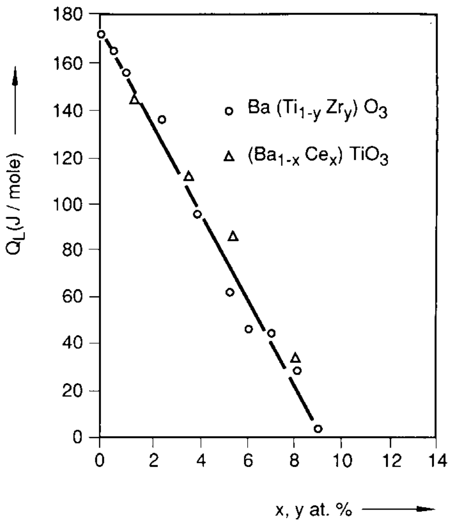
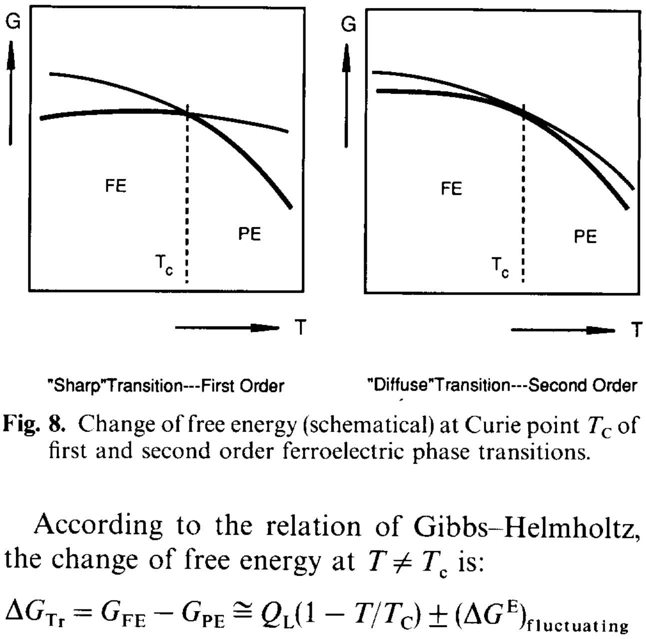


Fig. 7. Concentration dependence of the latent heat occurring at the Curie point of mixed crystals of $Ba(Ti_{1-y}Zr_y)O_3$ and $(Ba_{1-x}Ce_x)TiO_3$.



"Sharp"Transition---First Order "Diffuse"Transition---Second Order

Fig. 8. Change of free energy (schematical) at Curie point T_C of first and second order ferroelectric phase transitions.

According to the relation of Gibbs–Helmholtz, the change of free energy at $T \neq T_c$ is:

$$\Delta G_{Tr} = G_{FE} - G_{PE} \cong Q_L(1 - T/T_C) \pm (\Delta G^E)_{fluctuating}$$

First-order phase transitions exhibit a pronounced change of ΔG on both sides of T_c, which is determined by the height of $\Delta H_{Tr} = Q_L$. For a second-order phase transition ($Q_L = 0$) in contrast, ΔG changes very smoothly on both sides of T_c (see Fig. 8). Even small amounts of ΔG^E superimposing a second-order phase transition will therefore be able to produce a coexistence of ferroelectric and paraelectric phases (Fe⇔Pe) over a wide range of temperature ($T_c \pm \delta T$). The higher the latent heat Q_L, the smaller the influence of ΔG^E, and the narrower the range of coexisting ferroelectric and paraelectric phases: $\delta T \Rightarrow 0$.

Materials having 'diffuse' ferroelectric phase transitions show instead of a well-defined Curie point T_C a standard distribution of Curie points around a mean value of θ_C:

$$X(T_C) = (1/\sqrt{\pi s})\exp - ((T_C - \Theta_C)^2/s)$$

At small latent heats high standard deviations of T_C must be expected. In $Ba(Ti,Zr)O_3$ dielectrics with second-order phase transitions standard deviations of up to $\sqrt{s} \cong 30\,K$[8] were found.

6 Conclusions

In spite of the identical concentration dependence of $Q_L(x,y)$ found in mixed crystal ceramics of $Ba(Ti_{1-y}Zr_y)O_3$ and $(Ba_{1-x}Ce_x)TiO_3$, the effect of the grain growth anomaly on the dielectric maximum is completely different. The explanation of this phenomenon, however, is rather simple. In contrast to Q_L the concentration dependence of T_C differs considerably in both materials. In $Ba(Ti,Zr)O_3$ the depression of T_C is $\cong 5{\cdot}5\,°C/mol\%$ Zr, while that of Ce in $(Ba,Ce)TiO_3$ is $\cong 21\,°C/mol\%$. Hence, for reduction of T_C to room temperature c. 20 mol% Zr, but only 5 mol% Ce, are needed. In $(Ba_{1-x}Ce_x)TiO_3$ the phase transition is still first order ($Q_L \cong 75$ J/mol) at room temperature (20°C) (see Fig. 9), whereas in $Ba(Ti_{1-y}Zr_y)O_3$ second-order phase transitions appear for $T_C \leq 80\,°C$ ($y > 0{\cdot}09$).

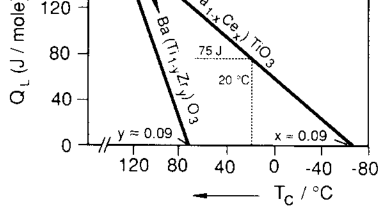


Fig. 9. Latent heat Q_L at the Curie points of $(Ba_{1-x}Ce_x)TiO_3$ and $Ba(Ti_{1-y}Zr_y)O_3$, plotted as function of T_C.

Because of the first-order phase transition the dielectric maximum of Ce-doped Y5V dielectrics is less sensitive to the grain growth anomaly than that of conventional Y5V materials, based on the classical system $(Ba,Ca)(Ti,Zr)O_3$. The following general conclusion can be drawn: donor-doped Y5V dielectrics should have a first-order phase transition slightly below room temperature ($T_C \cong 10\,°C$).

7 Applications of Ce-doped Dielectrics to Ceramic Multilayer Capacitors

With respect to the high endurance of donor-doped $BaTiO_3$, Ce-doped $BaTiO_3$ materials are expected to be suitable candidates for the manufacture of MLCCs with thin dielectric layers. Figure 10 shows the micrograph of a MLCC of 1 μF capacitance which has been sintered with 12 μm dielectric layers and Ag/Pd inner electrodes at 1300°C from Ce-donor doped material. Still at a grain size of 2–3 μm, the level of the dielectric Curie maximum is as high as $K \cong 11\,000$ at $T_C \cong 10\,°C$. Possibly due to a small number of electron compensated $Ce^{\bullet}$ donors, the insulation resistance is slightly lower than in conventional Y5V materials without donor dopant. As can be seen in Fig. 11, the endurance of Ce-doped MLCCs is outstanding on applying 'highly accelerated life tests' (HALT: 400V, 100°C). The insulation resistance of Ce-doped MLCCs (12 μm layers) was maintained unchanged over the whole testing period of 100 h. In contrast, MLCCs manufactured with 30 μm thick dielectric layers from conventional Mn-acceptor doped $(Ba,Ca).(Ti,Zr)O_3$ Y5V material showed strong degradation under the same testing conditions. The high endurance is considered to be a result of the low number of oxygen vacancies in the donor-doped $BaTiO_3$.

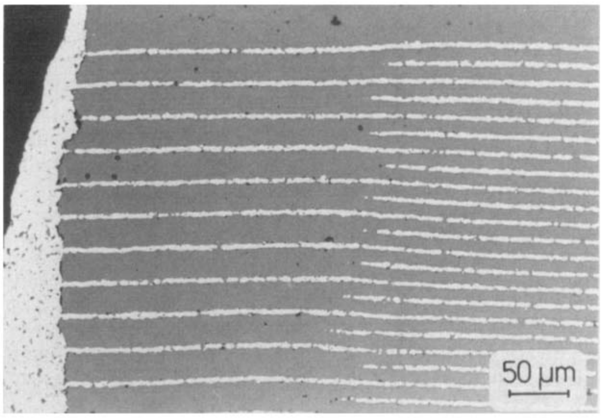


Fig. 10. MLCC showing 12 μm thick dielectric layers, made from CeO_2-doped $BaTiO_3$ ceramic.

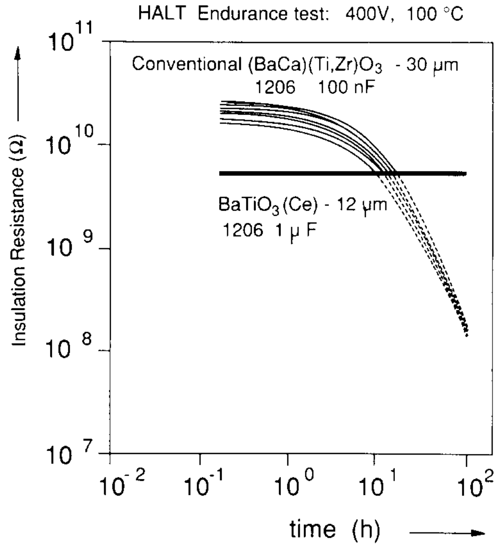


Fig. 11. Degradation behaviour of MLCCs, produced with 30 μm dielectric layer from conventional Mn-doped $(Ba,Ca)(Ti,Zr)O_3$ compared to MLCCs with 12 μm dielectric layer made from CeO_2-doped $BaTiO_3$.

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