Journal of the European Ceramic Society 21 (2001) 1637–1642

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Dielectric materials for sintering in reducing atmospheres

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Received 4 September 2000; received in revised form 23 October 2000; accepted 25 October 2000

Abstract

Ceramic multilayer capacitors (MLCC) with Ni base metal electrodes (BME) have nowadays achieved the standard of MLCCs with noble metal (Pd/Ag) electrodes. One of the greatest problems to be solved at the industrialization of BME capacitors was the suppression of the electrical degradation, caused by the mobility of charged oxygen vacancies. This paper gives a review of the research and development of BME materials © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$ and titanates; Capacitors; Defects; Lifetime

1. Introduction

Ceramic multilayer capacitors (MLCC) are one of the most important electronic components at the surface mounting of electronic circuits. Up until 1995 most MLCCs were manufactured with expensive inner electrodes of palladium or palladium silver alloys. Nowadays more than 60% of MLCCs are worldwide manufactured with Ni base metal electrodes (BME). The present importance of BME capacitors is based on the tremendous increase of the Pd price in the last few years. Between 1992 and 2000 the Pd price has increased by the factor of 10 and more. Compared to MLCCs with classical noble metal electrodes (Pd/Ag) cost savings of a factor of 2–5 are achieved using Ni inner electrodes. Especially the new generation of BME MLCCs, containing several hundreds of thin (< 4 μm) dielectric layers can be produced for an acceptable price only by the use of Ni inner electrodes.

This paper deals with a review of the history of BME capacitors which had already begun around the year 1960. The BME review is divided into three main sections:

1960–1980:	The BME pioneer phase.
1980–1990:	The first industrialization phase.
1990–2000:	The break-through.

A major problem of BME is that these capacitors must be fired in a reducing atmosphere to protect the Ni from oxidation. In reducing atmospheres barium titanate is slightly reduced, forming doubly ionized oxygen vacancies. The electrons make the reduced perovskite material highly semiconducting. So after sintering normal $BaTiO_3$ based dielectrics in forming gas (N_2/H_2) the insulation resistance (IR) decreases by 10–12 orders of magnitude.

$$BaTiO_3 + x\,H_2 \longrightarrow BaTiO_{3-x}[V_o]_x + xH_2O \qquad (1)$$

$$[V_o] \longrightarrow [V_o]^{\bullet\bullet} + 2e \qquad (2)$$

2. The pioneer phase 1960–1980

First solutions of the insulation problem have been already offered by Herbert[1] in the year 1962. Herbert[1] detected certain ions which could largely improve the IR of $BaTiO_3$ sintered in reducing atmosphere. In the years 1970–1976 the defect chemistry of donor and acceptor doped $BaTiO_3$ was thoroughly studied in the Philips Research Laboratories.[2–4] Daniels[3] observed that transition ions like Fe^{3+} Mn^{2+} and Cr^{3+} are strong electron acceptors on Ti-sites. Acceptors in the perovskite lattice of $BaTiO_3$ were generally found to be deep traps for conduction electrons.

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PII: S0955-2219(01)00082-6

$$A_{(\mathrm{TI})} + ne \rightarrow \left[A_{(\mathrm{TI})}\right]^{n'}$$
$$A = \mathrm{Cr}^{3+},\ \mathrm{Mn}^{2+},\ \mathrm{Mn}^{3+},\ \mathrm{Fe}^{3+}\ \text{etc.} \tag{3}$$

Acceptor doped $BaTiO_3$ fired in reducing atmosphere remains highly insulating up to temperatures of 350°C. The more acceptors are incorporated in the perovskite lattice, the more conduction electrons can be trapped and the lower the oxygen partial pressure can be adjusted at sintering of BME MLCCs (Fig. 1). At the end of the seventies the insulation problem of $BaTiO_3$ fired in reducing atmosphere seemed to be solved, so that the industrialization of BME was started in 1979.

3. First industrialisation of BME 1980–1990

In the years 1975–1980 a number of important BME patents have been filed. Only a small selection[5–7] is presented here. All inventions were based on $BaTiO_3$ and mixed crystals containing various kinds of acceptors ions. As one of the most effective acceptors Ca ions on Ti-sites, $[\mathrm{Ca}_{(\mathrm{Ti})}]''$, were found.[8,9] Ca is a common constituent of dielectric ceramics used in decoupling capacitors. In mixed crystals of the composition $(Ba,Ca)(Ti,Zr)O_3$ (BCTZ) the large Ca ions usually enter the Ba-sites. However, if the material contains excess of $BaCO_3$, then up to 4 mol% Ca^{2+} enters the Ti-sites[10] of the perovskite lattice. Slight changes of the A/B atomic ratio thus decide about the IR of BCTZ fired in reducing atmosphere.

$$(\mathrm{Ba,Ca})\mathrm{TiO_3} \xrightarrow{\mathrm{BaCO_3}} \mathrm{Ba(Ti,Ca)O_3} \tag{4}$$

The first years of the BME industrialization were characterized by severe quality crises. It had been overlooked that acceptor doped dielectrics exhibit a considerable ionic conductivity caused by the mobility of charged oxygen vacancies in the electric field. Already at room temperature the electromobility of $V_o^{\bullet\bullet}$ is rather high in $BaTiO_3$, thus giving rise to the phenomenon of electrical degradation.[11] The higher the acceptor concentration, the larger the number of ionized oxygen vacancies which lead to rapid degradation. Degradation turned out as the most critical BME problem, because these materials are always acceptor doped.

$$\left[\mathrm{Ca}_{(\mathrm{Ti})}\right]'' = \left[\mathrm{V}_{(\mathrm{o})}\right]^{\bullet\bullet} \tag{5}$$

In the year 1979 the US company Centralab launched a production of BME Y5V capacitors, based on Mn-acceptor doped BCTZ. Production and sale of the BME MLCCs had to be stopped rather quickly due to disastrous degradation of the IR. Already under moderate dc field and temperature stress the insulation resistance of these MLCCs broke abruptly down after few hours.

The life stability of BME MLCCs can be largely improved by a gentle re-oxidation treatment.[12,13] BME MLCCs sintered in an atmosphere of moist N_2/H_2 were, thereafter, heat-treated for a while at temperatures of 900–1100°C in an atmosphere, containing 50–100 ppm O_2. The oxygen partial pressure during re-oxidation must be low enough to prevent the Ni electrodes from severe oxidation. The plausible explanation for the improvement of life stability was that re-oxidation decreases the number of $[V_o]^{\bullet\bullet}$ in the BME material. Especially in the case of valence unstable acceptor ions, e.g. Cr^{3+}, Mn^{2+}, Fe^{2+}, the re-oxidation should alternate the valence state of the acceptor ions, e.g. Mn^{2+} to Mn^{3+} or Mn^{4+}, thus diminishing the number of $[V_o]^{\bullet\bullet}$, e.g:

$$\left[\mathrm{Mn}^{2+}\right]'' \approx 1[\mathrm{V_o}]^{\bullet\bullet},$$

$$\left[\mathrm{Mn}^{3+}\right]' \approx 1/2[\mathrm{V_o}]^{\bullet\bullet},$$

$$\left[\mathrm{Mn}^{4+}\right] \approx \text{nil}.$$

Thermogravimetric and magnetic investigations of Mn-doped $BaTiO_3$[14] revealed divalent Mn at firing conditions corresponding to those of BME sintering. In atmospheres containing 100 ppm O_2 at 1000°C a valence change from Mn^{2+} to Mn^{3+} occurs (Fig. 2). Large numbers of $[V_o]^{\bullet\bullet}$, therefore, still exist in re-oxidized BME material. Moreover, re-oxidation experiments on BME MLCCs at 1000°C showed that the re-oxidation process is totally controlled by the low oxygen partial pressure of the Ni/NiO equilibrium of 5×10^{-11} bar provided by the Ni inner electrodes. Nevertheless, a large improvement of the life stability was observed after re-oxidation. From this has been deduced that the strong improvement of life stability after re-oxidation cannot be simply assigned to annihilation of oxygen vacancies caused by the valence change of acceptor ions.

At the re-oxidation of BME materials a number of interesting phenomena can be observed. The ionized oxygen vacancies formed to compensate the charge of the acceptor ions show a strong trend to form clusters and dislocation loops. The dislocation loops look like little "coffee beans" in TEM (Fig. 3), and are highly mobile so that they are difficult to study in detail. Clustering of oxygen vacancies is obviously a transient phenomenon. Depending on the annealing conditions (time, temperature and oxygen partial pressure) the clusters appear and disappear in the BME material.

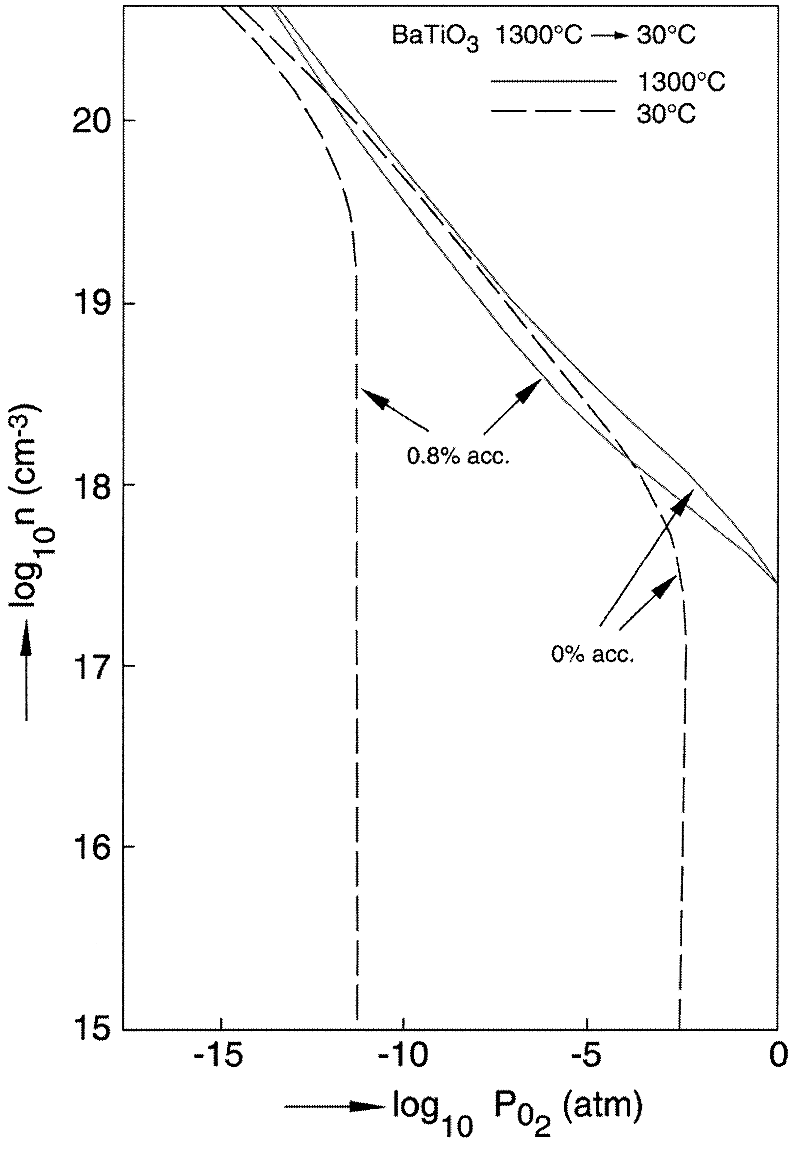

Fig. 1. Carrier concentration in undoped and acceptor doped $BaTiO_3$ as function of the oxygen partial pressure at room temperature and 1300°C. (Thesis: R.Wernicke[4].)

Clustering of oxygen vacancies seems to influence strongly the ferroelectric and dielectric properties of the BME material. In Yb-doped $Ba(Ti,Zr)O_3$, fired at 10^{-12} bar at 1300°C, the dielectric maximum increased almost by a factor of 2 after re-oxidation at 10^{-4} bar at 1000°C. It decreased, however, by a factor of 2 again after annealing in air.[15,16] The transient changes of the Curie maximum are probably due to interactions of $[V_o]^{\bullet\bullet}$ and acceptors with ferroelectric domains, which influence the mobility of ferroelectric domain walls and from that resulting the dielectric constants and losses. It should be noted, that Yb^{3+} is considered as a valence stable acceptor on Ti-sites. TGA confirmed that the number of oxygen vacancies did not change during re-oxidation treatment. From this has been concluded that re-oxidation mainly influences the mobility of $[V_o]^{\bullet\bullet}$.

4. The break-through of the BME technology 1990–2000

Compared to MLCCs prepared from donor-doped materials with Pd/Ag electrodes the life stability of re-oxidized Mn-doped BME MLCCs remained still somewhat poor. Around the year 1990 in Japan[17] a new generation of BME materials came up, showing excellent life stability which was comparable to that of air-fired materials. The new BME materials usually contained mixtures of donors and acceptors. Most probably based on the interaction of donors and acceptors, the electromigration of $[V_o]^{\bullet\bullet}$ has been largely suppressed in these materials. Donors and acceptors form together highly stable complexes which can no longer be oxidized even in pure oxygen atmosphere. The donors reduce the number of $[V_o]^{\bullet\bullet}$ and seem to act as strong barriers against electromigration of oxygen vacancies.

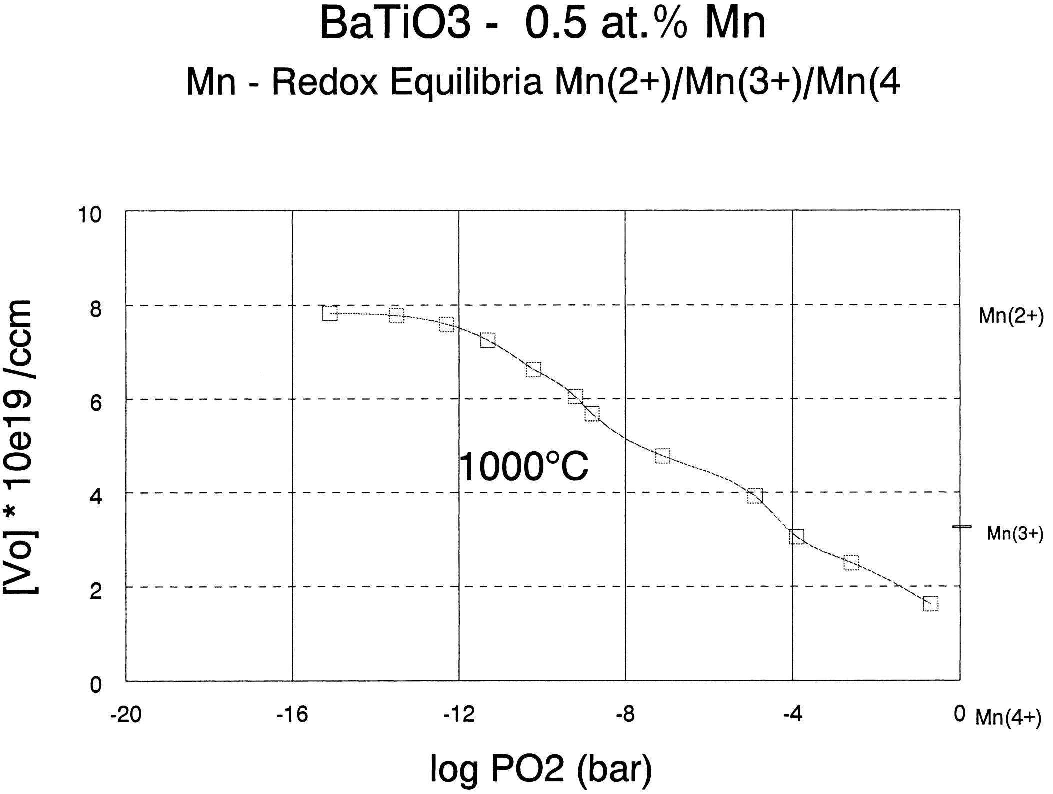

Fig. 2. Valence state of Mn and concentration of oxygen vacancies $\left(V^{\bullet\bullet}_{(o)}\right)$ in BaTiO$_3$ as function of the oxygen partial pressure.

$$\left[\mathrm{Mn}^{3+}_{(\mathrm{Ti})}\right]' + \left[\mathrm{Nb}^{5+}_{(\mathrm{Ti})}\right]^{\bullet} \rightarrow \left\{\left[\mathrm{Mn}^{3+}_{(\mathrm{Ti})}\right]\left[\mathrm{Nb}^{5+}_{(\mathrm{Ti})}\right]\right\}^{0} \qquad (6)$$

$$\left[\mathrm{Mn}^{2+}_{(\mathrm{Ti})}\right]'' + \left[\mathrm{W}^{6+}_{(\mathrm{Ti})}\right]^{\bullet\bullet} \rightarrow \left\{\left[\mathrm{Mn}^{2+}_{(\mathrm{Ti})}\right]\left[\mathrm{W}^{6+}_{(\mathrm{Ti})}\right]\right\}^{0} \qquad (7)$$

The interaction between donors and acceptors was found to be independent of the special nature of the ions and is only determined by the ionic charge of donors and acceptors.[18] From this has been derived that the interaction between donors and acceptors is widely controlled by electric fields.

4.1. The three magic ions Y, Dy and Ho

The most effective dopes to improve the life stability of BME materials are the so-called three "magic ions" Y^{3+}, Dy^{3+}, and Ho^{3+}. Similar to Ca^{2+} these ions have an amphoteric character and are thus able to enter the A-sites as well as the B-sites of the perovskite lattice[19] (Fig. 4). On the A-sites the magic ions act as donors, while they are acceptors on the B-sites. Depending on the A/B atomic ratio the donor or acceptor character prevails in the material. The magic ions seem to compensate each other on different lattice sites, forming donor acceptor complexes. The number of oxygen vacancies is, therefore, rather low. The life stability of BME materials containing donor-acceptor complexes

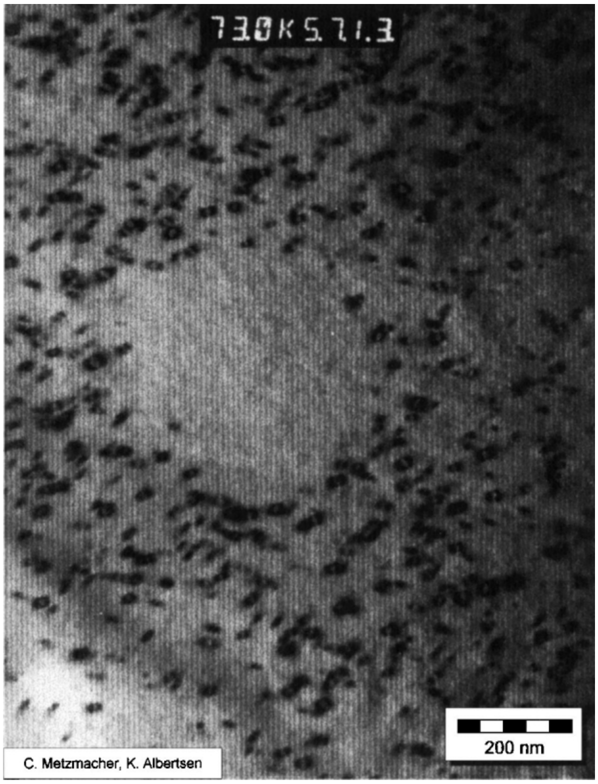

Fig. 3. TEM micrograph of oxygen vacancy clusters in acceptor doped BaTiO$_3$ sintered in reducing atmosphere (Courtesy of K. Albertsen and C. Metzmacher, Philips Research Laboratories).

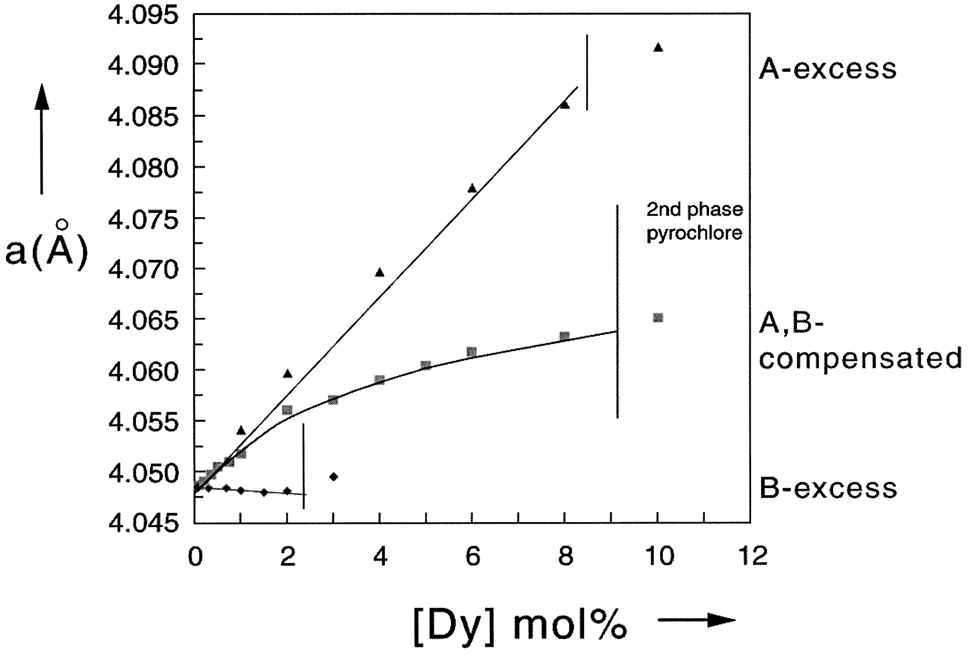

Fig. 4. Lattice parameters of $BaTiO_3$, containing Dy^{3+} on A-, B-, or on both A- and B-sites.

and one of the magic ions was found extremely high. In a 400 μm thick ceramic disc of Y/Nb-doped material no degradation could be observed after 800 h, applying a dc voltage of 950 V and a temperature of 350°C to the disc.

5. Outlook

The BME technology has become a mature technology and BME MLCCs are nowadays accepted worldwide even in high-grade devices. The performance of Ni BME capacitors has reached the standard of air fired MLCCs with Pd/Ag inner electrodes. BME MLCCs are specially attractive for MLCCs showing high capacitance values up to 100 μF. In such MLCCs the large number of inner electrodes makes the employment of cheep Ni inevitable. BME MLCCs exhibit a number of attractive advantages compared to Ta capacitors. The break-down voltage of MLCCs is much higher, the electrode series resistance (ESR) and the impedance at higher frequencies (> 100 KHz) are much lower than in Ta caps. It is, therefore, expected that BME MLCCs will soon replace the Ta electrolytic capacitors in the range 1–100 μF.

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