How Trivalent Amphoteric Dopants in BaTiO$_3$ Ceramics Improve Reliability of Capacitors

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Abstract. A new hypothesis regarding the role of rare earth dopants in improving the lifetime of multilayer capacitors with base metal electrodes is presented. The hypothesis is based on the experimental findings, which have shown that the site occupancy of the important dopants is a function of the overall A/B ratio in the perovskite dielectric material. The main assumption is that deviation from A/B stoichiometry significantly controls the mobility of oxygen vacancies along the grain boundaries.

INTRODUCTION

Traditionally, multilayer ceramic capacitors (MLCs) were made of successive layers of precious metal (Pt, Pd, Pd-Ag alloy) and barium titanate (BT). In order to reduce production costs, the precious metal electrodes are replaced by base metal electrodes (BME), Ni and Cu. BME are readily oxidized during the sintering (co firing) process under ambient conditions. It is therefore necessary to fire BME- MLCs in reducing atmospheres. This creates other problems, such as high dielectric losses and dielectric degradation, as the BT accommodates large concentration of oxygen vacancies and electrons when fired at low oxygen partial pressure. The electron concentration can be easily reduced by addition of acceptor impurities, such as Mn and Ca on the Ti site.[1,2] This suppresses the conductivity and contributes to dielectric loss. The concentration of oxygen vacancies is further enhanced by the addition of the acceptor dopants. The redistribution of oxygen vacancies under dc bias is responsible for failure mechanisms of the capacitors, as reported by a number of authors.[3]

Extensive experimental work done on that system have shown that addition of some trivalent dopants (so-called "magic dopants") to the BT can improve the lifetime.[4-6] Specifically, Y, Ho, Dy and sometimes Er and Gd can improve the lifetime under certain formulations and heat treatments. Other trivalent impurities do not demonstrate this marked improvement. Fundamental understanding of the role of these dopants is lacking. There exist two different models trying to explain the improvement in the lifetime of BME- MLCs. The A-site model[7] suggests that these dopants act as donors and improve reliability by reducing the concentration of oxygen vacancies. The B-site model[8] suggests that these dopants act as acceptors and improve reliability by

reducing the bulk diffusion of oxygen vacancies through strain and electric field interactions.

It was found,[9] using accurate X-Ray Diffraction (XRD) measurements,[10] that the main difference between the "magic dopants" and other trivalent dopants is that the "magic dopants" choose their site according to the A/B ratio and the oxygen partial pressure during the firing. Since site change of a well-defined valence dopant cause change of the relative charge, these dopants are called amphoteric. This is consistent with earlier conductivity measurements on air fired samples,[11] where it was shown that Er can occupy either A or B site depending on Ba-stoichiometry.

The experimental findings suggest that a new model is needed. It seems that A-site occupancy is not the preferential one for most of the "magic dopants" at A-rich compositions. This is true at least for the idealized compositions investigated by us.[9] On the other hand, if the B-site model is correct, some other dopants (Lu, Yb, Pr) are expected to improve the lifetime.

THEORETICAL CONSIDERATIONS OF SITE OCCUPANCY

In order to gain understanding on what influences the site occupancy ratio, we consider the following reaction:

$$R_{Ba}^{\bullet} + V_{Ti}^{''''} \Leftrightarrow R_{Ti}^{'} + V_{Ba}^{''} \tag{1}$$

and its corresponding mass action relation:

$$\frac{[R_{Ba}^{\bullet}]}{[R_{Ti}^{'}]} = K(R,T)\frac{[V_{Ba}^{''}]}{[V_{Ti}^{''''}]} \tag{2}$$

We use the Kröger-Vink notation[12] for point defects, and R represents a +3 cation. Eqs.(1),(2) hold only during the sintering, where these species are mobile enough to establish near equilibrium conditions.

From Eq.(2) it follows that Ba-rich phase drives the ratio towards B-site and vice versa. However, one has to remember that this is only a ratio, i.e., it can still be very close to zero or very large for a particular impurity R. Since the charge difference of trivalent ion is ±1 for both sites, it is expected that the ionic size will be the main factor influencing the magnitude of K. Large ions will tend to occupy the A-site (large K) and small ions will tend to occupy the B-site (K approaches zero). The influence of the stoichiometry is most significant in the cases where K is of comparable order of magnitude as the metal vacancy ratio. In addition, the metal vacancy ratio is $P(O_2)$ dependent. For simple cases, it is proportional to the oxygen vacancy concentration, as shown below.

The mass action relation in accordance with Schottky reaction is,

$$[V_{Ba}^{''}] \times [V_{Ti}^{''''}] \times [V_O^{\bullet\bullet}]^3 = K_S(T) \tag{3}$$

For the Ba-rich case the sample is in equilibrium with a phase of the type $(BaO)_k(TiO_2)_l$ where $k > l \geq 0$. Thus the chemical potential of the Ba in the BT phase is fixed (with respect to changes in the Ba/Ti ratio in the system) by the excess "BaO" from the adjacent phase, and we may write:

$$BaO \Leftrightarrow Ba_{Ba}^{\times} + O_O^{\times} + 2V_O^{\bullet\bullet} + V_{Ti}^{''''} \tag{4}$$
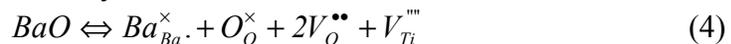
and hence:

$$[V_{Ti}''''] \times [V_O^{\bullet\bullet}]^2 = K_I(T) \tag{5}$$

Using Eqs.(3) and (5) we find that the ratio between the concentrations of the metal vacancies is proportional to the oxygen vacancy concentration:

$$\frac{[V_{Ba}'']}{[V_{Ti}'''']} = \frac{K_S}{K_I^2}[V_O^{\bullet\bullet}] \tag{6}$$

Again, it is important to emphasize that this is true only at high temperatures, i.e., during the sintering process. The same proportionality, with different constants, can be found for the Ti-rich case. The oxygen vacancy concentration is a decreasing function of P(O$_2$). Depending on the impurity concentration, it might be a very weak function over several orders of magnitude. Our studies with accurate x-ray diffraction demonstrate that the influence of the cation stoichiometry on site occupancy is indeed P(O$_2$) dependent, as suggested by combining Eqs.(2) and (6).

# NEW HYPOTHESIS ON THE ROLE OF AMPHOTERIC DEFECTS IN BME-MLC

Based on the experimental findings, we outline below a new hypothesis on the mechanism by which the "magic dopants" improve the lifetime of BME-MLCs. The amphoteric defects improve reliability by adding a degree of freedom to the system. By adding an impurity which can choose its site according to local deviations from stoichiometry, one effectively expands the barium titanate phase width and reduces space charge near the grain boundaries. In the extreme case of deviation from stoichiometry, segregation of Ba or Ti rich second phase is also inhibited. It is assumed (and yet should be checked experimentally) that the conductivity of oxygen along the grain boundaries is enhanced in the presence of space charge. This phenomenon is well known in other systems, such as:

1. Silver halides with alumina as a second minority phase.[13]
2. Chemical diffusion coefficient in transition metal oxides in the presence of insoluble second metal phase.[14]
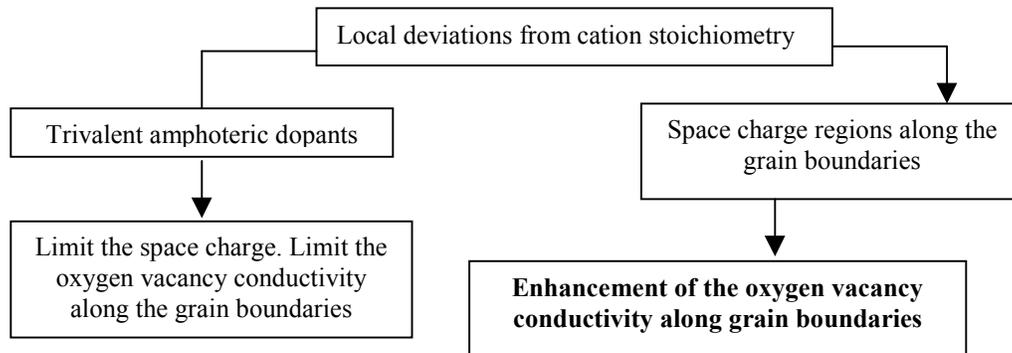
FIGURE 1. Graphic presentation of the new hypothesis

The assumption is, therefore, that amphoteric dopants prevent the enhancement of low temperature diffusion of oxygen vacancies along grain boundaries. This becomes even more important in reduced firing samples because the phase width of the BT becomes narrower at low $P(O_2)$ sintering. To show this let us consider the case where the system consists of two solid phases: BT and the next Ba-rich phase, namely, Ba_2TiO_4. In equilibrium one may write (as in Eq.(4)),

$$Ba_2TiO_4 \Leftrightarrow BaTiO_3 + 2V_O^{\bullet\bullet} + V_{Ti}^{''''} \tag{7}$$
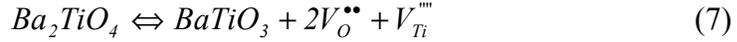
In terms of chemical potentials, this becomes,

$$\mu(Ba_2TiO_4) = \mu(BaTiO_3) + 2\mu(V_O^{\bullet\bullet}) + \mu(V_{Ti}^{''''}) \tag{8}$$

If only the BT phase exists, it means that the sum of the chemical potentials in the r.h.s. of Eq.(8) is less than the chemical potential of the second solid phase (l.h.s.). For that situation, reducing the oxygen partial pressure while keeping everything else constant results in more oxygen vacancies and therefore enhancement of the sum in the r.h.s.. Eventually, reducing the oxygen partial pressure may result in fulfilling the condition of Eq.(8) and hence precipitation of the second Ba-rich phase. The same consideration can be done for the Ti-rich case, with a similar result. The overall conclusion is that the phase width of BT is an increasing function of the oxygen partial pressure during the sintering.

CONCLUSIONS

1. Er, Y, Ho and Dy are amphoteric dopants in barium titanate fired at low $P(O_2)$, at high temperatures.
2. Larger RE ions occupy the A-site, as donors, and exhibit somewhat complex compensation mechanism, in relation to the $P(O_2)$ and Ba/Ti ratio during the firing. Smaller RE occupy the B site, as acceptors, and are compensated mainly by oxygen vacancies.
3. A new hypothesis regarding the role of the amphoteric dopants in improving the lifetime of BME-MLCs was presented. The main assumption is that deviation from A/B stoichiometry changes significantly the mobility of oxygen vacancies *along* the grain boundaries. The amphoteric dopants serve as buffers and maintain the overall A/B ratio close to one. The space charge near the grain boundaries is altered, and this may even inhibit second phase segregation in extreme cases.

ACKNOWLEDGMENT

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