



# Hydroxyl defect effect on the resistance degradation behavior in Y-doped (Ba,Ca)(Ti,Zr)O<sub>3</sub> bulk ceramics



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## ABSTRACT

Degradation behavior of acceptor (Y)-doped (Ba,Ca)(Ti,Zr)O<sub>3</sub> ceramics sintered in moist reducing atmosphere and subsequently re-oxidized in dry or wet atmospheres was contrasted. The degradation behavior critically depends on the water vapor incorporation, the time to degradation systematically decreased with the incorporation of hydroxyl defects (OH)<sub>o</sub><sup>•</sup>. The electrical conductivity was investigated by means of impedance spectroscopy (IS) to determine properties, such as grain and grain boundary conductivity, grain boundary potential barrier height, and space charge layer thickness. Furthermore, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) were applied to consider microstructure, microchemistry, and oxygen stoichiometry changes.

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## 1. Introduction

A complex composition with a mixture of amphoteric dopants, such as Y, Dy, Ho and co-doped acceptors, such as Mg, Mn, Cr, etc. formulates high-permittivity dielectrics for multilayer ceramic capacitors (MLCCs) with co-fired nickel (Ni) base metal electrodes (BME) [1,2]. Ni-MLCCs are commonly fired in reducing environment of moist mixtures of nitrogen and hydrogen (N<sub>2</sub>/H<sub>2</sub> + H<sub>2</sub>O) to prevent the oxidation of the Ni internal electrodes. In such reducing atmospheres, BaTiO<sub>3</sub> forms a large amount of positively charged oxygen vacancies V<sub>o</sub><sup>•</sup> as point defects that are electrically compensated by a high number of conduction electrons [3,4], which give rise to a dramatic decline of the insulation resistance (IR) by 10–12 orders of magnitude. Daniels [4] found that transition metal ions such as Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Cr<sup>3+</sup> act as strong electron acceptors on Ti-sites. The incorporation of acceptors has the effect of fixing concentration of the charged oxygen vacancies defects ([A'] ≈ 2[V<sub>o</sub><sup>•</sup>]), thereby suppressing the electron generation for improved insulation resistance. On the other hand, a rather high mobility of oxygen vacancies at high temperatures, generated by the incorporation of

acceptor dopants, in the presence of electric fields was considered to be responsible for the phenomenon of electrical degradation [5]. The most critical issue for acceptor doped Ni-MLCCs is electrical degradation, which is ascribed to a large amount of oxygen vacancies in the dielectric materials.

Life reliability of Ni-MLCCs could be improved by a slight re-oxidation treatment at temperatures between approximately 900 °C and 1000 °C within an atmosphere containing only very little oxygen [6]. The oxygen partial pressure during re-oxidation must be kept low enough to prevent the Ni inner electrodes from oxidation. It was plausibly explained that the life reliability improvement of Ni-MLCCs after re-oxidation results from the reduction of the number of oxygen vacancies [7]. However, this re-oxidation process is limited by the low oxygen partial pressure *p*(O<sub>2</sub>) of 5 × 10<sup>-11</sup> bar at 1000 °C for the Ni/NiO equilibrium, provided by the Ni inner electrodes [8]. Large numbers of oxygen vacancies therefore remain after the re-oxidation process. As for the commonly used valence instable acceptor ions, e.g. Mn<sup>3+</sup> or Cr<sup>3+</sup>, re-oxidation induces a valence change, e.g. Mn<sup>3+</sup> to Mn<sup>4+</sup>, thus diminishing the number of compensating oxygen vacancies. On the other hand, in the case of valence stable acceptors [9–12], such as Ca<sup>2+</sup>, and rare earth metal ions, such as Y<sup>3+</sup>, Sc<sup>3+</sup>, Dy<sup>3+</sup>, and Ho<sup>3+</sup> on the Ti-site do not alter their valence state. Therefore, the number of compensating oxygen vacancies remains unchanged after re-oxidation.

Acceptor-doped dielectric ceramics fired in moist atmospheres are expected to be impaired by the effect of hydroxyl defects incorporated in the perovskite lattice. Hydroxyl defects in BaTiO<sub>3</sub> were

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first found by Coufová *et al.* [13], who observed OH-stretch vibrations in BaTiO<sub>3</sub> single crystal. Stotz and Wagner [14] reported about hydroxyl defects replacing oxygen ions O<sup>2-</sup> in the sub-lattices of oxides as positively charged donors (OH)<sub>O</sub><sup>•</sup>. Large amount of hydroxyl defects were detected in freshly prepared hydrothermal BaTiO<sub>3</sub> powders, which could be removed as desorbed water on heating in air at temperatures above 300 °C [15]. Waser [16] studied absorption and desorption of D<sub>2</sub>O (heavy water) in BaTiO<sub>3</sub> at 900 °C. A strongly increasing solubility of (OD)<sub>O</sub><sup>•</sup> defects with increasing number of ionized oxygen vacancies could be detected, corresponding to an increasing concentration of acceptors. A negligible amount of oxygen vacancies was observed in donor-doped BaTiO<sub>3</sub>. Therefore, a strong relation between the formation of hydroxyl defects and oxygen vacancies was assumed. The effect of hydroxyl defects incorporated into the perovskite structure is also expected to modify the dielectric characteristics in acceptor-doped dielectric ceramics fired in moist atmosphere. Rare-earth acceptor-doped (Ba,Ca)(Ti,Zr)O<sub>3</sub> ceramics fired in reducing atmosphere showed significant changes of the dielectric characteristics after re-oxidation [17]. The height of the dielectric Curie maximum and the dissipation losses were significantly influenced by various treatments in dry or moist atmospheres [18].

A comparatively high mobility of ionized oxygen vacancies in an applied electrical field gives rise to a notable ionic conductivity in BaTiO<sub>3</sub> [19]. Hydroxyl ions (OH)<sub>O</sub><sup>•</sup> are considered to be too large for electro-migration. On the other hand, protons H<sup>+</sup> could move as interstitial defects through the oxygen sub-lattice easily [16]. Proton hopping is therefore assumed to give rise to a considerable contribution to the ionic conduction in BaTiO<sub>3</sub>, in addition to electro-mobility of charged oxygen vacancies. However, there are few reports that studied the effect of hydroxyl defects on the resistance degradation behavior.

The purpose of this study is to investigate the effect of hydroxyl defects on the resistance degradation behavior in Y-doped dielectric ceramics of the system (Ba,Ca)(Ti,Zr)O<sub>3</sub> (BCTZ), which have been fired under moist reducing conditions and afterwards re-oxidized at 1000 °C in various moist or dry atmospheres. It is well known that the ionic size is a main factor influencing the incorporation of rare-earth ions into BaTiO<sub>3</sub> ceramics [2,20–24]. Yttrium with an intermediate ionic size (0.90 Å) in BaTiO<sub>3</sub> occupies both A-site and B-site depending on the Ba/Ti ratio [25,26]. Slight excess of BaO guarantees exclusive incorporation on B-site [11]. In such materials the portion of the resistive grain boundary is much more significant in the specimens. Moreover, the effect of hydroxyl defects on the grain and grain boundary properties and its correlation with the degradation behavior was investigated by applying complex impedance spectroscopy (IS) analysis. Thus, we were able to clarify in details the reasons for the degradation behavior in Y-doped BCTZ with the incorporation of water vapor and point out the most important factors related to the degradation behavior.

## 2. Experimental procedure

### 2.1. Sample preparation

Dielectric powders of the nominal composition (Ba<sub>0.96</sub>Ca<sub>0.04</sub>)(Ti<sub>0.8125</sub>Y<sub>0.0075</sub>Zr<sub>0.18</sub>)<sub>0.995</sub>O<sub>3</sub> were prepared by the conventional solid state reaction method, using reagent grade BaCO<sub>3</sub> (Solvay 99%), CaCO<sub>3</sub> (Maruo Calcium Co. Ltd. 99%), TiO<sub>2</sub> (Showa Denko 99%), Y<sub>2</sub>O<sub>3</sub> (Rhodia 99%), and ZrO<sub>2</sub> (Daiichi Kigenso Kagaku Kogyo Co Ltd 99.9%) as raw materials. A slight excess of 0.5 mol% of the A-site ion Ba<sup>2+</sup> was employed in this formulation in order to assure the incorporation of the Y<sup>3+</sup> ion as Y<sub>Ti</sub><sup>'</sup> acceptor on the Ti-site. Similar compositions are commonly used in connection with the industrial production of dielectric materials showing the

**Table 1**  
Partial oxygen pressure of various heat-treatment conditions.

Heat-treatment condition		pO <sub>2</sub> (atm)
as fired	wet	3.9 × 10 <sup>-10</sup>
reox. 20.9% O <sub>2</sub> /N <sub>2</sub>	wet	1.8 × 10 <sup>-1</sup>
reox. 20.9% O <sub>2</sub> /N <sub>2</sub>	dry	1.7 × 10 <sup>-1</sup>
reox. 20.9% O <sub>2</sub> /N <sub>2</sub> (10H)	dry	1.7 × 10 <sup>-1</sup>

temperature specification of Y5V and a dielectric maximum at a temperature of approximately 20 °C. Before weighing, BaCO<sub>3</sub> was dried at 700 °C for 1 h in CO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were dried at 600 °C for 1 h in O<sub>2</sub>, ZrO<sub>2</sub> was dried at 500 °C for 1 h in O<sub>2</sub>, and CaCO<sub>3</sub> was dried at 400 °C for 1 h in CO<sub>2</sub> to ensure the compositional accuracy. The raw materials were intensively blended, mixed and milled for 24 h in a suspension with ethanol (solid content: 40%), using a polyethylene jar and Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> balls. The ball-milled slurries were then dried in a rotary evaporator and thereafter pulverized with an agate mortar before calcination. Calcination treatments were conducted at 1200 °C for 5 h in air. The calcined powders were mixed with 1 mol% SiO<sub>2</sub> as sintering aid, then ground in ethanol using a planetary mill, then followed by 24 h ball milling in a 500 ml polyethylene bottle partially filled with Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> balls (loading rate: 33%) of 2 mm in diameter. The powders obtained from the dried slurries were then granulated with PVA (Polyvinyl Alcohol) and pressed into bulk disks with ~8 mm in diameter and with ~0.7 mm in thickness applying a uniaxial pressure of 400 MPa. After burning out the PVA binder at 400 °C for 2 h in air, the disks were sintered at 1360 °C for 1 h in a moisturized gas mixture of N<sub>2</sub> with 1 vol% of H<sub>2</sub> that was saturated with water at 20 °C. The fired pellets were thereafter subjected for 2 h or 10 h to a re-oxidation treatment at 1000 °C in various atmospheres of wet or dry mixtures of N<sub>2</sub> with 20.9 vol% of O<sub>2</sub>. The values for the partial pressures of oxygen were shown in Table 1. Katsu [27] indicated that an oxygen vacancy would only need 0.2 s to migrate at 900 °C along a diffusion path of 20 μm by using  $d = \sqrt{D(T) \times t}$ , where  $d$  is the diffusion path length,  $D(T)$  is the diffusion coefficient, and  $t$  is the equilibration time. Therefore, soaking at 1000 °C with 2 h is sufficient for defect chemical equilibria to be established during re-oxidation in this study. The specimens were slowly cooled down in the furnace in the re-oxidation atmosphere. According to the slow cooling in the furnace it is expected that water vapor can penetrate the ceramics for a longer period at temperatures below 500 °C. No difference of oxygen partial pressures between wet and dry conditions could be measured by a calibrated oxygen sensor.

According to the hydration experiments on rare-earth doped BaZrO<sub>3</sub> of Kreuer *et al.* [28], a saturation of the ceramics with water vapor,  $p(\text{H}_2\text{O}) = 23$  mbar, can be expected at  $T < 400$  °C. The temperature dependence of water uptake is determined by the kind and concentration of the acceptor dope as well as the basic composition of the perovskite phase.

### 2.2. Sample characterization

The sintered bulk ceramics were characterized by scanning electron microscope (SEM), high-resolution transmission electron microscopy (HR-TEM), and electron energy loss spectroscopy (EELS). SEM imaging of polished and thermally etched ceramics surface was performed using a Hitachi S4100 SEM (Ibaraki, Japan) operated with an accelerating voltage of 20 kV in a secondary electron-imaging mode. The microstructure and microchemistry of the dielectrics were also analyzed using a Hitachi HF-3300 field emission TEM (Ibaraki, Japan) operated at 200 kV equipped with a Gatan GIF EEL Spectrometer (Pleasanton, USA). The energy resolution at zero-loss peak is about 0.6 eV (full width at half maximum).

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