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Mechanism of Improvement of Resistance Degradation in Y-doped BaTiO3 Based MLCCs with Ni Electrodes under Highly Accelerated Life Testing

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Abstract

The mechanism of improvement of resistance degradation in Y-doped $BaTiO_3$ based multilayer ceramic capacitors (MLCCs) with Ni electrodes has been studied using electrical measurement techniques, minor phase identification and the measurement of oxygen vacancy concentration. Admittance spectroscopy and thermally stimulated current measurements show the relaxation due to barium vacancy states caused by Y doping. The minor phase identification by XRD indicated those Y^{3+} substitutes for perovskite A-site. Oxygen vacancy concentration measurement indicated that Y decreases the oxygen ion vacancy concentration in $BaTiO_3$. These results suggest that Y^{3+} acts as a donor and creates barium vacancies, which compensate for the oxygen vacancies and thereby improve the resistance degradation. © 1999 Published by Elsevier Science Limited. All rights reserved

Keywords: Ni electrode; defects; lifetime; $BaTiO_3$ and titanates; capacitors.

1 Introduction

The high volumetric efficiency of multilayer ceramic capacitors (MLCCs) has made them valuable components in electronics, where constant downsizing has become the norm. Central to the continued cost-effectiveness of MLCCs has been the use of Ni electrodes, which, however, has necessitated compositional modifications to combat the degradation of insulation resistance resulting from sintering in reducing atmospheres. The authors have previously found that resistance degradation measured in highly accelerated life tests (HALT) was caused by oxygen ion vacancy migration. The oxygen ion vacancies were created by MnO substitution to prevent a reduction of insulation resistance. Furthermore, the authors have reported that donor doping such as Y^{3+} for $BaTiO_3$-based ceramics is an excellent method for improving the resistance degradation in HALT for Ni electrode MLCCs.[1–5] It is thought that the reduction in resistance degradation in HALT was due to the compensation of oxygen vacancies by barium vacancies, which in turn were created by Y^{3+} addition; the proposed process can be summarized as follows:

$$\mathrm{BaTiO_3{+}\delta MnO} \rightarrow \mathrm{Ba(Ti_{1-x}Mn''_{Ti\delta})O_{3-\delta}} + \delta\mathrm{TiO_2} \tag{1}$$

$$\mathrm{Ba(Ti_{1-\delta}Mn''_{Ti})O_{3-\delta}} + x/2\mathrm{Y_2O_3} \rightarrow \mathrm{(Ba_{1-x}Y^{\bullet}_{Bax})(Ti_{1-\delta}Mn''_{Ti\delta})O_{3-\delta+x/2}} + x\mathrm{BaO} \tag{2}$$

Recently, Randall and Shrout proposed a new hypothesis to explain the improvement of the life time in HALT.[6] In their model, Y^{3+} substitutes at the perovskite B-site as an acceptor and these result in a higher local stability of the oxygen ion vacancy through electrostatic interactions during HALT. The reason for Y^{3+} substituting at the perovskite B-site expected by the decrease of lattice energy at the oxygen ion vacancy site. Since the unit cell of perovskite can be expected to shrink due to oxygen ion vacancy formation, and to expand by B-site occupation of Y, the total lattice energy decreases.

The objective of this study was to clarify whether

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Y^{3+} assumes a donor or acceptor role when substituted into $BaTiO_3$-based materials using admittance spectroscopy, minor phase identification by XRD, and oxygen ion vacancy concentration determination by gravimetric analysis.

2 Experimental Procedure

The dielectric compositions for electrical measurement were $(Ba_{1-x}Ca_x)_m(Ti_{1-y}Zr_yO_2)$ + aMnO + bSiO$_2$ (BCTZ system) with $x=0$–$0{\cdot}07$, $y=0{\cdot}18$, $m=1{\cdot}004$, $a=0{\cdot}24$ mol%, $b=0{\cdot}2$ wt%, while Y_2O_3 was added in the same atomic ratio as MnO. $BaTiO_3$, $BaZrO_3$ and $CaTiO_3$ starting materials were highly pure hydrothermally synthesized powders. The other powders were reagent grade oxides or carbonates. The raw mixtures were prepared by wet ball-milling for 16 h using 10 mm and 3 mm ϕZrO_2 balls. MLCCs were prepared by the so-called sheet methods. Green sheets, which controlled between 15 and 30 μm, were formed by doctor blade casting. After casting, Ni electrodes were printed using a screen printing system. Next, 4 layers of the sheets were stacked, laminated, and cut into green chips. Binder burnout was followed by sintering between 1220 and 1340°C. During sintering, the oxygen partial pressure was controlled between 10^{-8} and 10^{-13} MPa by adjusting the amounts of H_2 and H_2O in the N_2-H_2-H_2O gas mixture. The chips were then annealed between 700 and 1100°C in 10^{-4} and 10^{-7} MPa PO_2 in order to reoxidize the dielectrics. Admittance spectroscopy was measured from 1 mHz to 1 MHz at 1 V_{rms}.

The compositions for the minor phase identification and gravimetric analysis were: Ba_m-$TiO_3 + x1/2Y_2O_3 + y$MnO with $m=1{\cdot}010$, $1{\cdot}000$, $0{\cdot}9950$, $x=0{\cdot}5$, $1{\cdot}0$, $1{\cdot}5$ at%, $y=0{\cdot}5$ at%. A/B-ratio in $BaTiO_3$ was corrected using X-ray fluorescence analysis. The raw mixtures were prepared by wet ball-milling for 16 h using 10 and 3 mm ZrO_2 balls. After drying, the processed powder was pressed with an organic binder into 12 mm disks, and the binder was burned out. The disks were sintered at 1400°C with O_2 atmosphere. X-ray powder diffraction analysis 2 theta was carried out in the range from 25 to 30°C in order to identify of minor phases caused by the substitution of excess Ba, Ti or Y in $BaTiO_3$. For the gravimetric analysis, polished samples (1 to 2 g) were used. The change in the oxygen ion vacancy concentration due to annealing at 1000°C in different oxygen partial pressure ($Po_2 = 1{*}10^{-15}$ to $1{*}10^{-6}$ MPa) was determined after quenching the samples to room temperature. The change in oxygen-ion vacancy concentration was determined by eqn (3)[7]

$$\Delta[Vo^{\cdot\cdot}] = \Delta m/m(\rho N_A/M) \qquad (3)$$

Where $\rho = 6$g/cm^3 (density of the sample), $N_A = 6{*}10^{23}$ mol^{-1} (Avogadro's number), $M = 16$ g/mol (atomic weight of oxygen), and $\Delta m/m$ = relative weight change.

3 Results and Discussion

Figure 1 shows the admittance spectra of Y^{3+}-doped and non-Y^{3+}-doped BCTZ systems. Three relaxation were observed in the low frequency range, with activation energies of 0·4, 0·8, and 0·8–0·9 eV, labeled δ,ζ and η, respectively. Their relaxation time were $5{*}10^{-1}$, $5{*}10^{3}$ and $3{*}10^{7}$ s, respectively, which indicate relaxation due to deep level states. Relaxation of peak ζ and η were not influenced by Y^{3+}-doping. Therefore, these may be related to acceptor states such as Mn_{Ti}'' and Ti''. On the other hand, the peak δ appeared with Y^{3+}-doping and disappeared under low PO_2 annealing as shown in Fig. 2. Thus, the reason for the behavior of this relaxation δ is assumed to be defects in BCTZ, which originate from either Y^{3+} doping or high PO_2 annealing. Since, Ba^{2+} vacancies (V_{Ba}'') are created by Y^{3+} substitution at the perovskite A-sites as well as by annealing under high PO_2 in

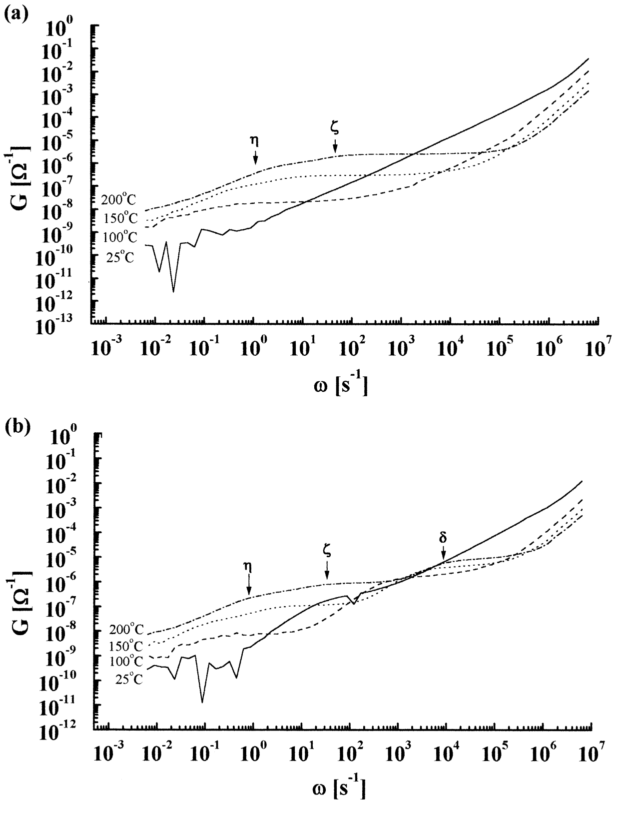

Fig. 1. (a) Admittance spectroscopy in non-Y^{3+}–doped BCTZ system annealed under $4{*}10^{-7}$ MPa partial pressure of oxygen. (b) Amittance spectroscopy in Y^{3+} –doped BCTZ system annealed under $4{*}10^{-7}$ MPa partial pressure of oxygen.

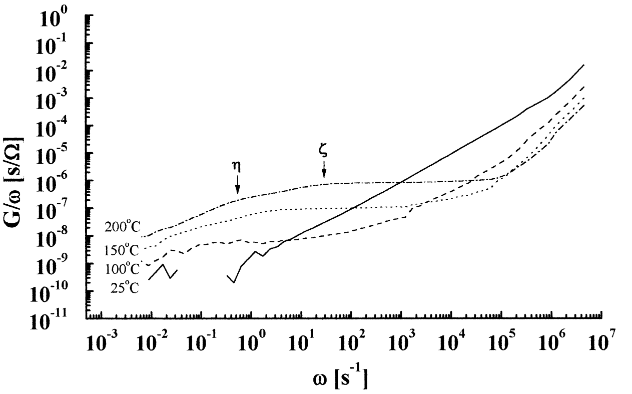

Fig. 2. Admittance spectroscopy in Y^{3+}-doped BCTZ system annealed under $3*10^{-8}$ MPa partial pressure of oxygen.

accordance with the Kröger–Vink diagram, and following equations.

$$\mathrm{BaTiO_3} + \frac{x}{2}\mathrm{Y_2O_3} \rightarrow (\mathrm{Ba}_{1-3x/2}\mathrm{Y}^{\bullet}_{\mathrm{Ba}x}\mathrm{V}_{\mathrm{Ba}x/2})$$
$$\mathrm{TiO_3} + 3x + \frac{3x}{2}\mathrm{BaO} \qquad (4)$$

$$\mathrm{BaTiO_3} + \frac{x}{2}\mathrm{O_2} \rightarrow (\mathrm{BaV}''_{\mathrm{Ba}x})\mathrm{TiO}_{3+x} + 2xh^{\bullet} \qquad (5)$$

Thus these results support that the relaxation at peak δ is originated from Ba^{2+} vacancies states (V''_{Ba}). The relaxation at 0·4 eV is expected from the transition of an electron from the valence band to the V_{Ba} site. The relaxation at peak δ in the admittance spectroscopy data, because of the strong dependence on Y^{3+}-doping and the annealing atmosphere is due to Ba^{2+} vacancies.

The authors have examined minor phase identification for $BaTiO_3$ and Y_2O_3 reaction in order to investigate the Y^{3+} occupation site for $BaTiO_3$. When Y_2O_3 substitutes the perovskite A-site or B-site, excess minor phases are released from $BaTiO_3$ according to following equations.

A-site substitution:

$$\mathrm{BaTiO_3} + \frac{x}{2}\mathrm{Y_2O_3} \rightarrow$$
$$(\mathrm{Ba}_{1-3x/2}\mathrm{Y}^{\bullet}_{Bax}V''_{Bax/2}) \qquad (6)$$
$$\mathrm{TiO_3} + 3x + \frac{3x}{2}\mathrm{BaO}$$

B-site substitution:

$$\mathrm{BaTiO_3} + \frac{x}{2}\mathrm{Y_2O_3} \rightarrow \mathrm{Ba}(\mathrm{Ti}_{1-x}\mathrm{Y}'_{\mathrm{Ti}x})\mathrm{O}_{3-x/2} + x\mathrm{TiO_2} \qquad (7)$$

Therefore, if Ba rich or Ti rich minor phases were identified, Y^{3+} occupation site can be determined.

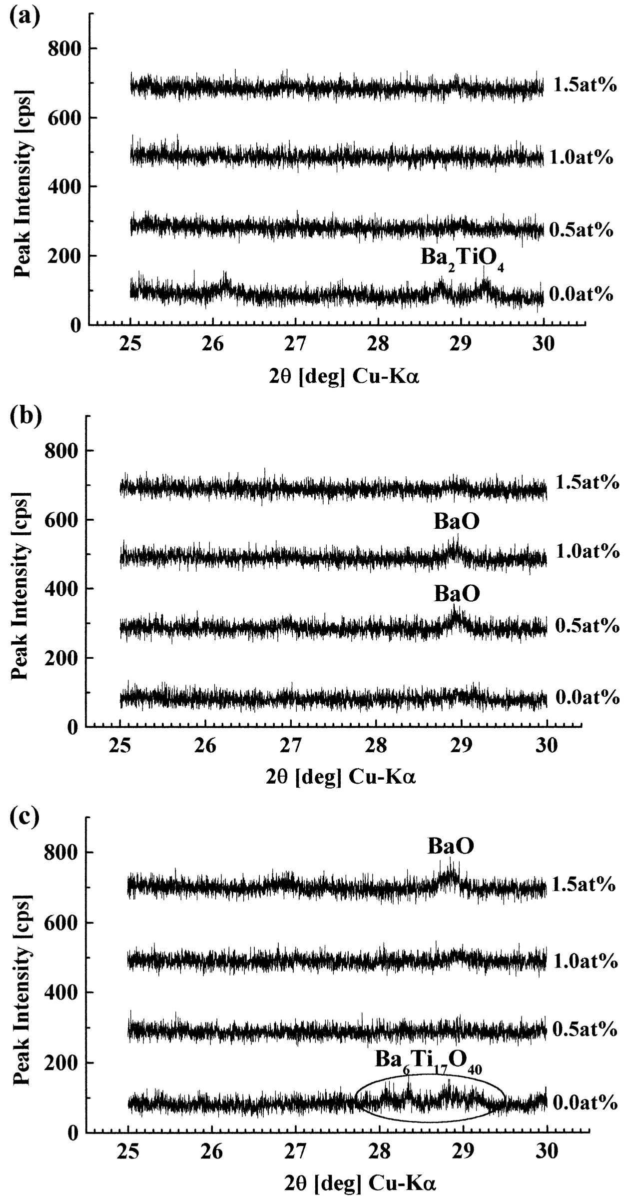

Fig. 3. (a) XRD profile of $BaTiO_3$ ($A/B = 1{\cdot}01$) + Y_2O_3 composition for various Y doping. (b) XRD profile of $BaTiO_3$ ($A/B = 1{\cdot}00$) + Y_2O_3 composition for various Y doping. (c) XRD profile of $BaTiO_3$ ($A/B = 0{\cdot}99$) + Y_2O_3 composition for various Y doping.

Figure 3 shows the minor phase identifications using XRD for $BaTiO_3$ with several A/B-ratios and Y_2O_3 doping. In the case of $BaTiO_3$ with A/B = 0·99, Ti-rich $Ba_6Ti_{17}O_{40}$ was identified in non- Y^{3+}-doped $BaTiO_3$. $Ba_6Ti_{17}O_{40}$ phase decreased with Y^{3+} doping, and the amount of BaO found at 1·5 at% Y^{3+} doped $BaTiO_3$. The resulting (Ba + Y)/Ti (= A/B) ratio is larger than unity. In the case of $BaTiO_3$ with $A/B = 1.00$, Ti or Ba-rich minor phase could not be found in non-Y^{3+}-doped $BaTiO_3$, and BaO appeared with Y^{3+} doping below 1·5 at%. However, BaO decreased again with excess Y^{3+} doping above 1·5 at%. Furthermore, in $BaTiO_3$ until $A/B = 1{\cdot}01$, Ba-rich Ba_2TiO_4 disappeared by Y doping. These result indicated that Y^{3+} substitutes perovskite A-site when (Ba + Y)/Ti ratio is smaller than 1·01, and perovskite B-site under extremely A-site rich condition. These phenomena are in agreement with eqn (7). Therefore, it is considered that Y^{3+} substitutes perovskite A-site and acts as a donor dopant while A/B-ratio smaller than unity.

Figure 4 shows the change in oxygen ion vacancy concentration for Y^{3+}, Mn^{+2} and Y^{3+}-Mn^{+2} doped $BaTiO_3$ under various oxygen partial pressures at 1000°C as determined by gravimetric analysis. Oxygen ion vacancy concentration of Mn^{+2} doped $BaTiO_3$ increased with decreasing oxygen partial pressures. On the other hand, oxygen ion vacancy concentration of Y^{3+} doped $BaTiO_3$ is independent of oxygen partial pressure. In the case of Y^{3+} and Mn^{2+} doped $BaTiO_3$, the influence of oxygen partial pressure decreased. These results indicated that Y^{3+} acts as a donor in $BaTiO_3$ under reducing atmosphere to compensate oxygen ion vacancies. Compensation of oxygen ion vacancies decreases in $BaTiO_3$ with $A/B = 1{\cdot}01$. The reason for this decrease may be due to B-site substitution of Y^{3+} into $BaTiO_3$. This would agree with minor phase identification. However, these results also indicated that Y^{3+} substitutes the B-site only partially and can behave both as a donor and an acceptor dopant in the $A/B > 1$ region.

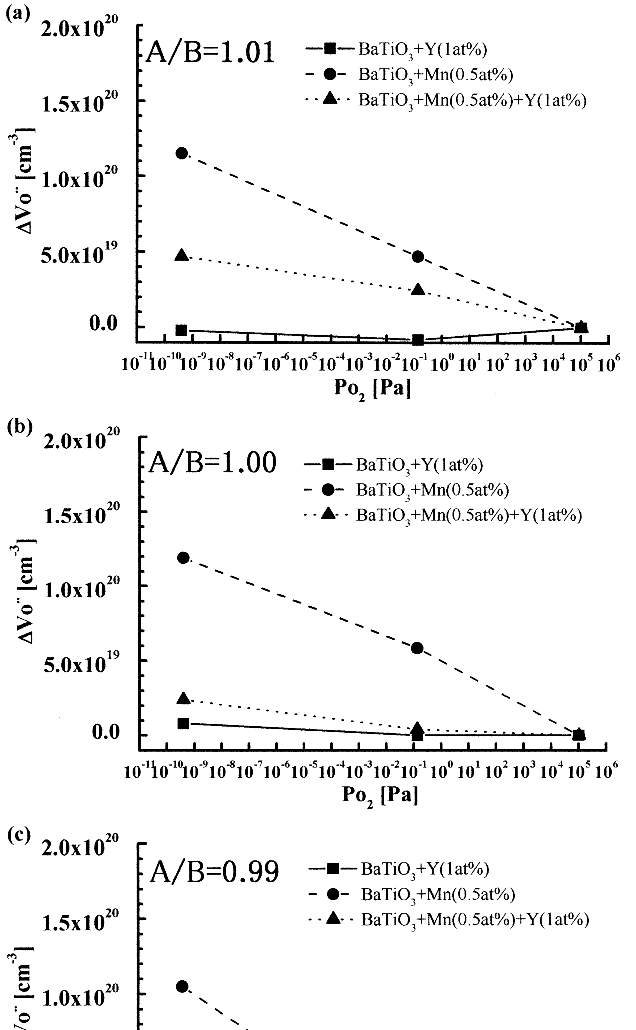

Fig. 4. (a) The change in oxygen ion vacancy concentration for Y^{3+}, Mn^{2+} and $Y^{3+}-Mn^{2+}$ doped $BaTiO_3$ under various oxygen partial pressure. (b) The change in oxygen ion vacancy concentration for Y^{3+}, Mn^{2+} and $Y^{3+}-Mn^{2+}$ doped $BaTiO_3$ under various oxygen partial pressure. (c) The change in oxygen ion vacancy concentration for Y^{3+}, Mn^{2+} and $Y^{3+}-Mn^{2+}$ doped $BaTiO_3$ under various oxygen partial pressure.

For commercial applications, additives such as SiO_2, Al_2O_3 were added to the $BaTiO_3$ in order to reduce the sintering temperature. SiO_2 and Al_2O_3 also create minor phases such as Ba_2TiSiO_3 and reduce the A/B-ratio. This is because, excess TiO_2 is released according following equation when Ba_2TiSiO_3 react with $BaTiO_3$ and SiO_2.

$$2BaTiO_3 + 2SiO_2 \rightarrow Ba_2TiSi_2O_8 + TiO_2 \qquad (8)$$

For this reason, the grain boundary near the minor phases indicate a Ti-rich composition.[3–5] Thus, actual A/B-ratio (including additives) for commercial compositions is usually smaller than unity according to following equations:

$$Ba_{1{\cdot}004}TiO_3 + aMnO \rightarrow Ba_{1{\cdot}004}(TiMn)_{(1+a)}O_{3-a} \qquad (9)$$

$$Ba_{1{\cdot}004}TiO_3 + \frac{b}{2}Y_2O_3 \rightarrow (BaY)_{(1{\cdot}004+b)}TiO_{3+3b/2} \qquad (10)$$

$$Ba_{1{\cdot}004}TiO_3 + 2cSiO_2 \rightarrow Ba_{(1{\cdot}004-2c)}Ti_{(1-c)}O_{3-4c} + cBa_2TiSi_2O_8 \qquad (11)$$

Actual A/B in $Ba_{1{\cdot}004}TiO_3 + aMnO + b/2Y_2O_3 + cSiO_2$ $(1{\cdot}004 + b\text{-}2c)/(1 + a\text{-}c)$, Thus, with:

$a = b = 0{\cdot}0025$
$c = 0{\cdot}0040$ (0·2 wt%) $A/B = 0{\cdot}9921$
$c = 0{\cdot}0010$ (0·05 wt%) $A/B = 1{\cdot}0009$
$c = 0{\cdot}0005$ (0·0025 wt%) $A/B = 1{\cdot}0025$

It can be assumed that most of Y_{3+} substitutes perovskite A-site and acts as a donor in commercial compositions, because minor phase identification and gravimetric analysis have shown that with A/B-ratio 1·00 Y^{3+} substitute perovskite A-site. Therefore, the effect of Y^{3+} addition in the BCTZ system supports our previous hypothesis shown in the following equations:

$$BaTiO_3 + \delta MnO + x/2Y_2O_3 \rightarrow (Ba_{1-x}Y^{\bullet}_{Bax})(TiMn''_{Ti\delta})O_{3-\delta+x/2} + xBaO + \delta TiO_2$$
$$\text{N.B. } V_{Ba} + V_{O}^{\cdot\cdot} \rightarrow n \qquad (12)$$

The insulation resistance degraded by the migration of oxygen vacancies from anode to cathode. $BaTiO_3$-based dielectrics for MLCCs often contain MnO in order to prevent the reduction during low PO_2 sintering. The Mn^{2+} is considered to act as an acceptor dopant, which induces oxygen vacancies during sintering. On the other hand, the addition of a donor such as Y^{3+} to $BaTiO_3$-based materials is thought to create Ba^{2-} vacancies, which compensate for the oxygen ion vacancies generated by acceptor doping. Thus, the authors again propose the following mechanism for the improvement of degradation of insulation resistance: a decrease in oxygen ion vacancy concentration resulting from donor doping improves the lifetime of $BaTiO_3$-based dielectrics for MLCCs in HALT.

4 Conclusions

The mechanism of improvement of resistance degradation in Y-doped $BaTiO_3$-based multilayer ceramic capacitors with Ni electrodes under highly accelerated life testing was studied and the following conclusions were obtained:

1. Three types of relaxation in BCTZ system were observed in admittance spectroscopy. The relaxation at 0·4 eV is expected V''_{Ba} site due to Y^{3+} doping. The relaxation at 0·8 and 0·8–0·9 eV are considered to originate from the Mn_{Ti}''-site.
2. It is clear that Y occupies perovskite A-site under $A/B \leqq 1{\cdot}00$, and perovskite B-site under $A/B > 1$ using minor phase identification. It is considered that most Y^{3+} substitutes A-site in $BaTiO_3$ and acts as a donor dopant in commercially available compositions because the actual A/B-ratio of commercial compositions is usually smaller than unity due to sintering aid such as SiO_2.
3. The effect of Y^{3+} addition on the compensation of oxygen ion vacancies could be detected using gravimetric analysis. Oxygen ion vacancy concentration decreased by Y^{3+} doping in A/B-ratio$\leqq 1$. At $A/B > 1$, the oxygen ion vacancies concentration decreased only partially due to Y^{3+} behaving as a donor dopant in B-site occupation according to minor phase identification.
4. The results mentioned above that Y^{3+} doped into $BaTiO_3$-based materials acted as a donor and creates V''_{Ba}, which compensated for the oxygen ion vacancies generated by acceptor doping, such as MnO. Y^{3+} doping and the creation of V''_{Ba} is considered to improve the lifetime in HALT

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