

# Effect of re-oxidation on dielectric properties in Ni-MLCC

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**Abstract** The effect of re-oxidation treatment on the solubility of dopants and the dielectric properties of rare-earths (La, Ho) and V-substituted BaTiO<sub>3</sub> solid solutions, assuming the shell phase of X7R dielectrics, was investigated. Ho-V-substituted samples showed larger increase of the lattice parameter and  $T_c$  by re-oxidation treatment compared with La-V-substituted samples. Electron spin resonance measurements revealed that the oxidation of V<sup>3+</sup> to V<sup>4+</sup> or V<sup>5+</sup> appeared in the range in which the increase of lattice parameter by re-oxidation treatment was observed. This suggests that the increase of  $T_c$  is due to the change of preferential occupational site of Ho ion from *A*-site to *B*-site, being accompanied with the oxidation of V<sup>3+</sup>. We also investigated the effect of re-oxidation treatment on the electrical properties and microstructure in Ni-MLCC samples, using rare-earths (La, Ho, Yb) and acceptors (Mn, V) doped BaTiO<sub>3</sub> based X7R dielectrics. The change in temperature characteristic of the dielectric constant by re-oxidation treatment was observed for the MLCC samples containing V with smaller content. In the case of Ho-V- and Yb-V-doped samples showed larger increase of the dielectric constant at around 120 °C compared with La-V-doped samples. The relationship between the microstructure and electrical properties of the MLCC sample was investigated by impedance measurement at elevated temperature.

**Keywords** Rare-earth · BaTiO<sub>3</sub> · Dielectric properties · Capacitors · Re-oxidation

## 1 Introduction

In recent years, multilayer ceramic capacitors (MLCCs) with Ni internal electrodes composed of more than 800 dielectric layers of about 1 μm thickness have been mass-produced. To produce such thin-dielectric-layer MLCCs with highly reliable electrical characteristics, many studies have been done on the dielectric materials focusing on the degradation mechanism. [1] In nonreducible BaTiO<sub>3</sub> (BT, ABO<sub>3</sub>) based dielectric materials used for Ni-MLCCs, it is well known that the resistance degradation of dielectrics strongly depends on the *A/B* molar ratio and the ratio of donor dopant to acceptor dopant. [2, 3] Saito et al. reported that highly reliable Ni-MLCCs conforming to X7R specification were obtained, using Ho and Mg doped BT based dielectrics, in combination with a re-oxidation treatment at the cooling stage below 1,000 °C during in the firing process. [4] Resistivities of the dielectrics were increased by the addition of Ho<sub>2</sub>O<sub>3</sub> when they were treated in an oxidizing atmosphere in the cooling stage. Kishi et al. reported the solubility of Mg and the rare-earth oxides (R<sub>2</sub>O<sub>3</sub>) into BT lattice. [1, 5] It was confirmed that Mg ions occupied the *B*-sites (acted as acceptors), larger ions (La, Sm) predominantly occupied the *A*-sites (acted as donors), smaller ions (Yb) predominantly occupied the *B*-sites (acted as acceptors), and intermediate ions (Dy, Ho, Er) occupied both the *A* and *B*-sites (acted as both donors and acceptors).

Mg, Mn and V ions are commonly used as acceptor dopants for nonreducible BT based dielectrics. Mn<sup>2+</sup> and V<sup>3+</sup> are easily oxidized by re-oxidation treatment, while Mg maintaining a constant valency 2+. Albertsen et al. reported

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the changes in the Curie point ( $T_c$ ) and the sample length under reduction and re-oxidation of BT ceramics containing Mn acceptors and various donor dopants on  $B$ -sites. [6] With increasing donor concentration, both the differences of the  $T_c$  and the sample length between the reduced and the re-oxidized state decreased. They deduced that the formation of donor-acceptor complexes suppressed the valence change of  $Mn^{2+}$  to  $Mn^{3+}$  or  $Mn^{4+}$ .

We previously reported the effect of re-oxidation treatment on the dielectric properties and the solubility in dopants in various rare-earths- and (Mg, Mn)-substituted BT. [7, 9] In the case of smaller ionic size rare-earths (Dy, Ho, Er, Yb)- and Mn-substituted samples, we confirmed that the decrease of the lattice parameter and a shift of  $T_c$  to higher temperatures due to oxidation of  $Mn^{2+}$  by re-oxidation treatment was observed in the range in which the rare-earth ions preferentially occupied  $B$ -sites. It was determined that the occupational sites of rare-earth ions in BT lattice strongly affected the valence state of acceptors and dielectric properties.

However, re-oxidation behavior of the dielectric properties in Ni-MLCCs has not been systematically reported so far. Therefore, in the present study, using valence-unstable V acceptor, we investigated the effect of re-oxidation treatment on the solubility of dopants and the dielectric properties of rare-earth (La, Ho) and V-substituted BT solid solutions, assuming the shell phase of X7R dielectrics compared with BT- $R_2O_3$ -MnO solid solutions. To clarify the effect of the site occupancy of rare-earths in BT lattice on the re-oxidation behavior in Ni-MLCCs, we also investigated the re-oxidation treatment on the electrical properties and microstructure in Ni-MLCC samples, using rare-earths (La, Ho, Yb) and acceptors (Mn, V) doped BT based X7R dielectrics.

## 2 Experimental

### 2.1 Rare-earths and V- substituted BT solid solutions

To examine the dielectric properties and the solubility in the shell phase of BT-  $R_2O_3$ - $V_2O_3$ -based X7R dielectrics, the samples were prepared according to the formula  $(Ba_{1-x}R_x)(Ti_{1-x}V_x)O_3$ ; where  $R = La, Ho, x=0\sim 0.10$ . This formula is based on a model substituting rare-earth and V ions for Ba and Ti, respectively. The raw materials,  $BaCO_3$ ,  $TiO_2$ ,  $R_2O_3$  and  $V_2O_3$  were mixed and then calcined at 1,250 °C. The calcined powder containing an organic binder was pressed into the disks, and then the disks were fired at 1,380 °C in a low oxygen atmosphere controlled by  $H_2$ ,  $N_2$ ,  $O_2$  and  $H_2O$  ( $P_{O_2}$  of approximately  $10^{-11}$ Pa) after the binder was burned out. Re-oxidation of the disks was carried out at 1,250 °C in

air. The microstructures of the sintered samples were observed by scanning electron microscopy (SEM). Liquid In-Ga was applied to opposite surfaces of the disks as electrodes and the capacitance of the reduced and the re-oxidized state samples was measured at 1 kHz, 1.0 Vrms using an LCR meter (HP-4284A), covering the temperature range from -55 to 150 °C. The ceramics were crushed and ground into a powder, and the identification of the crystalline phases and the phase transition of the samples were characterized by powder XRD analysis and differential scanning calorimetry (DSC), respectively. The occupational site of rare-earth element was determined by the behavior of the lattice parameters as a function of the doping amount  $x$ . In order to avoid the influence on the lattice parameters by phase transition, high-temperature powder XRD analysis was carried out at a higher temperature (300 °C) than the  $T_c$ . The lattice parameters were determined precisely using the whole-powder-pattern decomposition method (WPPD) [10] program as described in the previous paper. [11] The valence state of V ions of the samples was confirmed by X band electron spin resonance (ESR) measurement.

### 2.2 MLCC samples

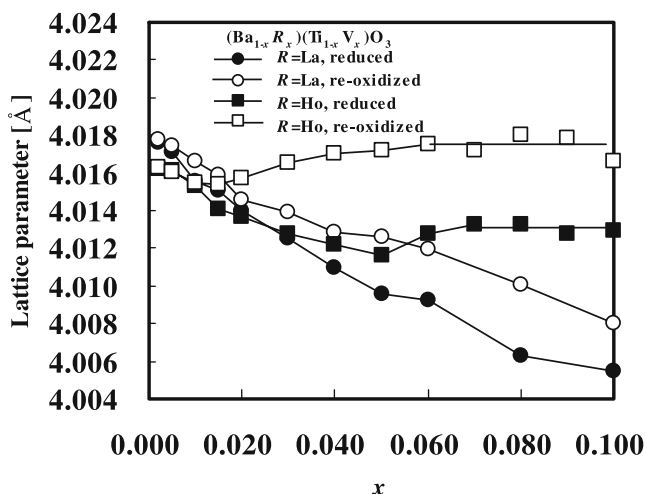
The effect of re-oxidation treatment on the dielectric properties of rare-earths (La, Ho, Yb) and acceptor (V, Mn) doped BT based X7R MLCCs were examined. The samples were prepared by the conventional method as follows. Hydrothermally synthesized BT with a mean particle size of about 0.35  $\mu m$  (Sakai Chemical Industry Co., Ltd.), reagent grade MgO, MnO,  $V_2O_3$ , rare earth oxides ( $La_2O_3$ ,  $Ho_2O_3$ ,  $Yb_2O_3$ ) and  $BaSiO_3$  as a sintering aid were weighed. They were mixed by ball milling for 15 h and then dried. MLCC samples were prepared by the so-called green-sheet method. Eleven green sheets (4  $\mu m$ ), on which printed Ni internal electrodes, as well as the protective sheets at the upper and lower sides were stacked and pressed into a bar and then cut into pieces. Terminal Ni electrodes were formed on both sides of the chips. The MLCC samples were fired at 1,240 °C in a reducing atmosphere controlled by  $H_2$ ,  $N_2$ ,  $O_2$  and  $H_2O$ . Re-oxidation treatment for MLCC samples was carried out at 1,000 °C in a weakly oxidizing atmosphere ( $P_{(O_2)}=30$ Pa). The microstructures of the samples were observed by SEM and transmission electron microscope (TEM). The capacitance of the MLCC samples was measured at 1 kHz, 1.0 Vrms using an LCR meter. The frequency response of impedance was measured at 160~300 °C and analyzed using an impedance/gain-phase analyzer (SI1260; Solartron Instrument, Ins., USA) and electrochemical impedance software (Zplot for Windows and Zview for Windows; Scribner Associates, Inc., USA).

### 3 Results and discussion

#### 3.1 Solubility and dielectric properties of rare earth- and V- substituted BT

The effect of re-oxidation treatment on the solubility of dopants in La-V- and Ho-V-substituted BT solid solutions was investigated. The crystalline phases of the reduced and the re-oxidized state samples were analyzed by XRD. In the case of the reduced state La-V-substituted samples, a single phase of BT solid solution was obtained up to  $x=0.050$ . As a secondary phase,  $\text{BaVO}_3$  or  $\text{Ba}_3(\text{VO}_4)_2$  (BV phase) appeared from  $x=0.060$ . On the other hand, in the case of the reduced state Ho-V-substituted samples, a single phase of BT solid solution was only obtained up to  $x=0.020$ . As a secondary phases, pyrochlore ( $\text{Ho}_2\text{Ti}_2\text{O}_7$ ) and BV phase appeared from  $x=0.030$  and  $x=0.060$ , respectively. By re-oxidation treatment, BV phase appeared from  $x=0.030$  for both La-V- and Ho-V-substituted samples.

The ionic radii of Ba, Ti, La, Ho and V are summarized as follows: *A*-site (12 coordinate):  $\text{Ba}^{2+}=1.610 \text{ \AA}$ ,  $\text{La}^{3+}=1.360 \text{ \AA}$ ,  $\text{Ho}^{3+}=1.234 \text{ \AA}$ ; and *B*-site (six coordinate):  $\text{Ti}^{4+}=0.605 \text{ \AA}$ ,  $\text{La}^{3+}=1.032 \text{ \AA}$ ,  $\text{Ho}^{3+}=0.901 \text{ \AA}$ ,  $\text{V}^{3+}=0.640 \text{ \AA}$ ,  $\text{V}^{4+}=0.580 \text{ \AA}$ ,  $\text{V}^{5+}=0.540 \text{ \AA}$ . The ionic radii of Ho ions in a 12-coordinate system are based on the relationship between coordination number and effective ionic radii according to Shannon's table. [12] The occupational sites were determined based on the change of the lattice parameter as follows. The increase in lattice parameter is based on *B*-site replacement with cations ( $\text{Ho}^{3+}$ ,  $\text{V}^{3+}$ ) larger than Ti ions. The decrease in lattice parameter is based on *A*-site replacement with cations ( $\text{La}^{3+}$ ,  $\text{Ho}^{3+}$ ) smaller than Ba ions, and *B*-site replacement with cations ( $\text{V}^{4+}$ ,  $\text{V}^{5+}$ ) smaller than Ti ions. Figure 1 shows the lattice parameters of the samples measured at 300 °C, as determined by WPPD. In the case of La-V-substituted



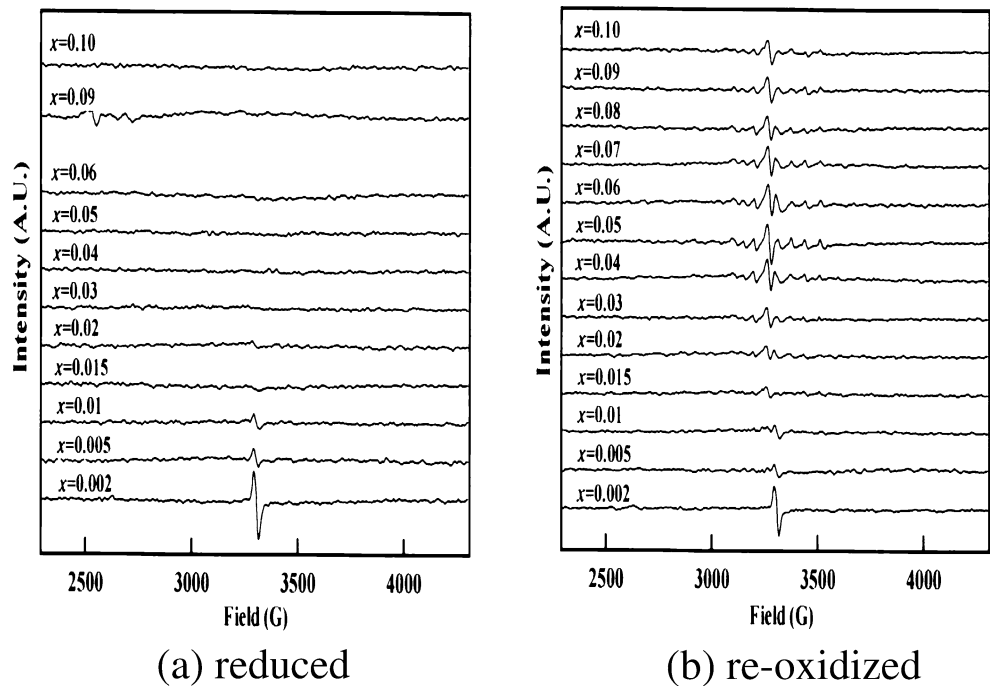
**Fig. 1** Lattice parameters of  $(\text{Ba}_{1-x}\text{R}_x)(\text{Ti}_{1-x}\text{V}_x)\text{O}_3$  solid solutions measured at 300 °C ( $R = \text{La}, \text{Ho}$ )

samples, the lattice parameter decreased monotonously as a function  $x$ , although the increase of the lattice parameter was observed by re-oxidation treatment. This indicated that La ions predominantly occupied the *A*-site. In the case of the reduced state Ho-V-substituted samples, the decrease and the increase of lattice parameter were observed. The change of the lattice parameter for the reduced state Ho-V-substituted samples is considered as follows. In the first stage, Ho mainly occupied the *A*-site accompanied by *B*-site occupation of  $\text{V}^{3+}$  ions, and then preferential occupational site of Ho ions in BT lattice changed from *A*-site to *B*-site along with precipitation of BV phase in the second stage. The difference of lattice parameter between the reduced and the re-oxidized state Ho-V-substituted samples was observed above  $x=0.015$ . The increase of the lattice parameter by re-oxidation treatment increased with increasing doped content up to  $x=0.060$  and then they showed no change up to  $x=0.100$ . This behavior is clearly different from the previous result for Ho-Mn-substituted BT solid solutions, which shows the decrease of the lattice parameter caused by oxidation of Mn. [7–9]

To clarify the effect of V on the lattice parameter, the valency of V was examined. Ho-V-substituted samples showed the change of valency of V by re-oxidation, while La-V-substituted samples showed no change. Figure 2 shows ESR spectra of Ho-V-substituted samples. In the case of the re-oxidized state samples, ESR spectra of  $\text{V}^{4+}$  appeared above  $x=0.015$ . The intensity of ESR spectra of  $\text{V}^{4+}$  increased with increasing doped content up to  $x=0.050$  and then they showed little change. This indicated that a portion of doped  $\text{V}^{3+}$  ions was oxidized to  $\text{V}^{4+}$  or  $\text{V}^{5+}$ . It seems that the change of the lattice parameter closely related to the valence change of V. However, the lattice parameter of the re-oxidized samples increased while the ionic radius of V decreased due to the valence change. In the case of Ho-Mn-substituted samples, we reported that Ho-donor- Mn-acceptor complexes are formed in the range in which Ho ions mainly occupy *A*-sites, so that oxidation of  $\text{Mn}^{2+}$  is prevented, and in the range in which Ho ions mainly occupy *B*-sites, increased Ho-acceptors bring about an increase in the amount of free  $\text{Mn}^{2+}$  which can be oxidized to  $\text{Mn}^{3+}$  or  $\text{Mn}^{4+}$  during the re-oxidation. Thus, in the case of Ho-V-substituted samples, it is considered that the increase of the lattice parameter by re-oxidation in the range above  $x=0.015$  is due to the change of preferential occupational site of Ho from *A*-site to *B*-site along with precipitation of BV phase, so that oxidation of  $\text{V}^{3+}$  to  $\text{V}^{4+}$  or  $\text{V}^{5+}$  increases with increasing Ho-acceptors.

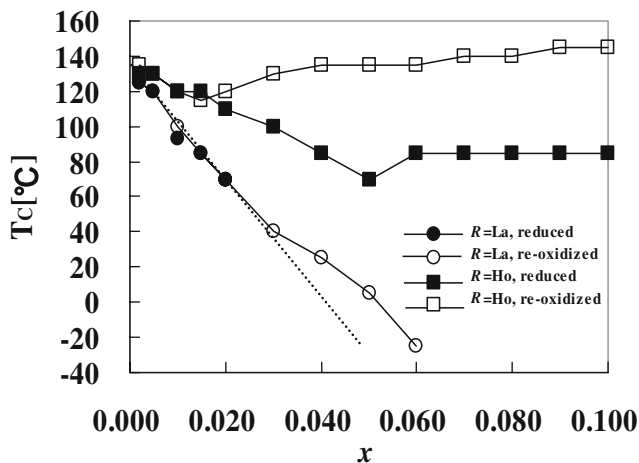
The  $T_c$  of the reduced and the re-oxidized state samples was determined by DSC and dielectric measurement. DSC was carried out for the samples with lower electrical resistivities, for which it is impossible to measure dielectric properties. Figure 3 shows the  $T_c$  shift of the reduced and the re-oxidized state samples. In the case of La-V-substituted

**Fig. 2** ESR spectra of  $(\text{Ba}_{1-x}\text{Ho}_x)(\text{Ti}_{1-x}\text{V}_x)\text{O}_3$  solid solutions as function of  $x$ . **(a)** reduced state, **(b)** re-oxidized state



samples,  $T_c$  decreased monotonously with increasing doped content, and the slope of  $T_c$  change for the re-oxidized state samples decreased above  $x=0.03$  compared with the extrapolated line from the data for the reduced state samples below  $x=0.02$ . It seems that the  $T_c$  of La-V-substituted samples increased slightly by re-oxidation treatment, although the data for the reduced state sample above  $x=0.03$  could not be obtained. On the other hand, Ho-V-substituted samples showed a large difference in the  $T_c$  shift by re-oxidation treatment. The increase of  $T_c$  by re-oxidation was observed above  $x=0.015$  and increased with increasing doped content

up to  $x=0.050$ , and then they showed a little change up to  $x=0.100$ . These results also correspond well with the results of the lattice parameters and the valency of V. Thus, it is considered that the decrease of  $T_c$  is attributed to  $A$ -site occupation of rare-earth ion for all the samples, and the increase of  $T_c$  is due to the change of preferential occupational site of Ho ion from  $A$ -site to  $B$ -site for both the reduced and the re-oxidized state Ho-V-substituted samples. Furthermore, it is expected that the valence change of V also influence the  $T_c$  of the re-oxidized state samples. Sinclair and Attfield reported that  $T_c$  of ferroelectric  $\text{ATiO}_3$  materials shows linear increase with  $A$ -cation size variance. [13] In the case of Ho-V-substituted samples, it is suggested that the increase in  $T_c$  is related to the increase of both  $A$ - and  $B$ -cation size variance due to the change in the occupational site ratio of Ho ion in BT lattice. As a result, it was confirmed that the site occupancy of the rare-earth ions strongly influenced the re-oxidation behavior, such as the  $T_c$  shift and the valence state of acceptor ions.

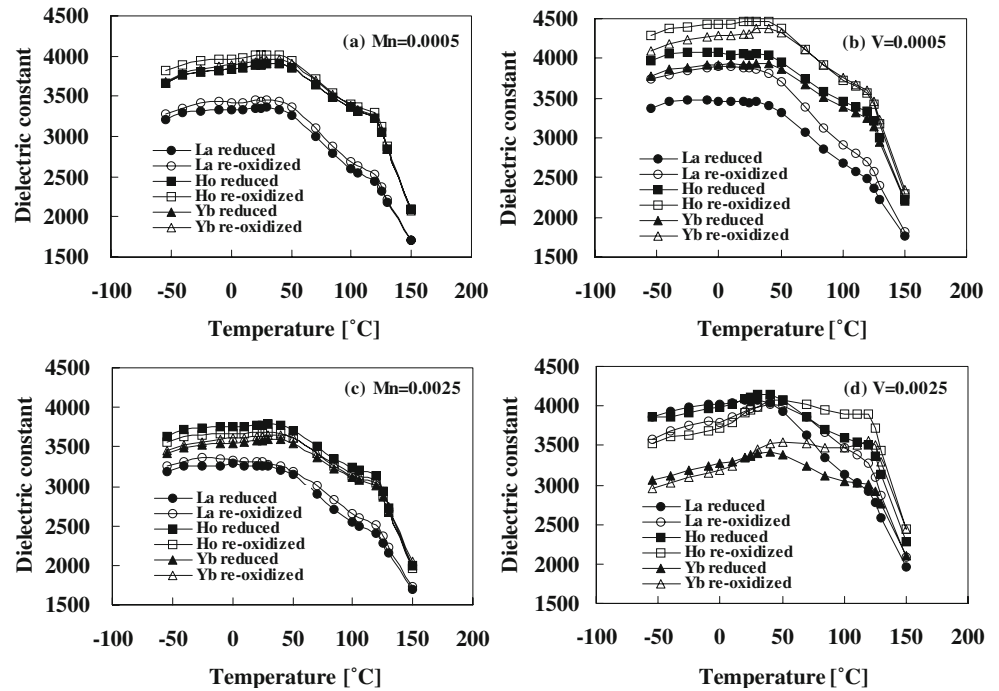


**Fig. 3** The change in  $T_c$  of the reduced and the re-oxidized state  $(\text{Ba}_{1-x}\text{R}_x)(\text{Ti}_{1-x}\text{V}_x)\text{O}_3$  solid solutions. ( $R = \text{La}, \text{Ho}$ ) (Dotted line: extrapolated from the data for the reduced state sample)

### 3.2 Effect of re-oxidation on dielectric properties in MLCCs

The effect of re-oxidation treatment on the electrical properties and microstructure in Ni-MLCC samples was examined, using three kinds of rare-earth elements having large different ionic radii (La, Ho and Yb) and valence unstable acceptors (Mn, V) doped BT based X7R dielectrics. All the samples showed core-shell structure with grain size about  $0.35 \mu\text{m}$  and showed no change in the

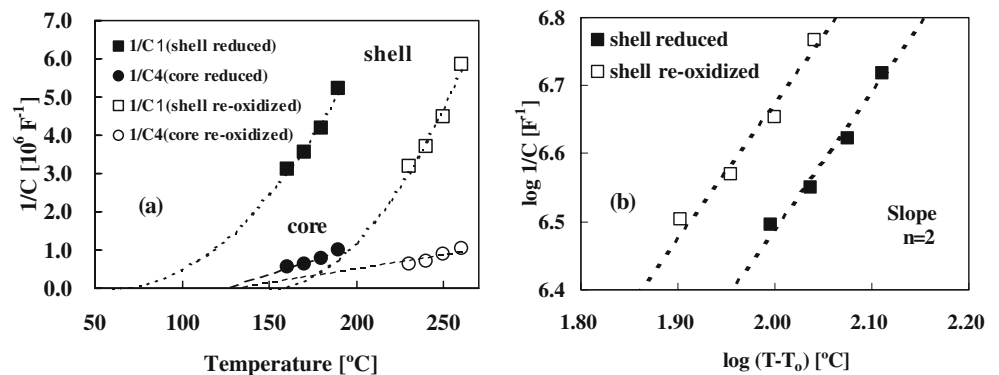
**Fig. 4** Temperature dependence of dielectric constant for the reduced and the re-oxidized state BT-MgO- $R_2O_3$  based X7R MLCC samples with various acceptors content. (a) Mn=0.05 atomic%, (b) V=0.05 atomic%, (c) Mn=0.25 atomic%, (d) V=0.25 atomic%, ( $R = La, Ho, Yb$ )



microstructure by re-oxidation. Figure 4 shows the temperature dependence of dielectric constant for the reduced and the re-oxidized state MLCC samples with different acceptor content. In the case of  $R$ -Mn-doped samples, all the samples showed little change in dielectric characteristics by re-oxidation. On the other hand,  $R$ -V-doped samples showed larger difference in the dielectric characteristics by re-oxidation. This can be attributed to the difference in the valence stability between Mn and V against re-oxidation condition for MLCC samples. The samples containing 0.05 atomic% V showed the increase of dielectric constant at lower temperature below 130 °C. In the case of the samples containing 0.25 atomic% V, all the samples showed the decrease of dielectric constants below room temperature and the increase of those at the temperature range between 40 and 130 °C. Especially, Ho-V- and Yb-V-doped samples

showed larger increase of the dielectric constant at around 120 °C compared with La-V-doped samples. This result showed same tendency as the result for  $R$ -V-substituted BT solid solutions which shown above. It is well known that dielectric constant of X7R dielectrics is the sum of those of the core phase (almost pure BaTiO<sub>3</sub>) showing dielectric Curie maximum around 125 °C and the shell phase (solid solution of BaTiO<sub>3</sub> and dopants) showing dielectric Curie maximum at a lower temperature. [14] Thus, the change in dielectric constant at a lower temperature of the X7R samples by re-oxidation treatment was attributed to the change in that of the shell phase. It is also expected that the increase of the dielectric constant at higher temperature region is based on the  $T_c$  shift to higher temperatures of the shell phase and the increase of dielectric constant of core phase. The present results revealed that valence-unstable V

**Fig. 5** Reciprocal capacitance of BT-MgO-Ho<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>3</sub> based X7R MLCCs as a function of temperature. (V=0.25 atomic%) (a)  $1/C$  vs. temperature, (b)  $\log 1/C$  vs.  $\log (T-T_0)$  plot





strongly affected the change in dielectric properties of the shell phase of X7R dielectrics by re-oxidation treatment compared with Mn acceptor.

We previously reported that the impedance data of X7R Ni-MLCC based on BT-MgO-Ho<sub>2</sub>O<sub>3</sub> dielectrics could be fitted to a 4-RC section electrical equivalent network, and correlated to the microstructure: the core phase, the shell phase, the grain boundary and the ceramic/electrode interface region. [15] Therefore, further investigation by introducing impedance measurement at elevated temperature was carried out to correlate the change in dielectric properties by re-oxidation to the microstructure, using the reduced and the re-oxidized state Ho-V-doped BT based X7R MLCC samples. It was also found that the impedance was successfully described using a 4RC-equivalent circuit in the present MLCC samples, and each capacitance element could be correlated to the microstructure from its behavior. Figure 5(a) shows the reciprocal capacitance against temperature for the core phase and the shell phase of the reduced and the re-oxidized state MLCC samples containing 0.25 atomic% V. It is well known that the core phase behaves as normal ferroelectrics, and the shell phase behaves as relaxor in BT-MgO-Ho<sub>2</sub>O<sub>3</sub> based X7R dielectrics. [16] Thus, it is expected that the reciprocal capacitance of the core phase and the shell phase follow Curie–Weiss law:  $\varepsilon=C/(T-T_0)^n$  ( $n=1$ : normal ferroelectrics,  $n=2$ : relaxor), where  $\varepsilon$  and  $C$  denote the dielectric constant and the Curie constant. [17] Figure 5(b) shows the  $\log 1/C$  vs.  $\log (T-T_0)$  plot for the data of the shell phase. As shown in Fig. 5(b), the data for the shell phase can be fitted as  $n=2$ . Thus, in the case of Ho-V-doped BT based MLCC samples, it was confirmed that the core phase behaves as normal ferroelectrics, and the shell phase behaves as relaxor. It was also found that the  $T_c$  of the shell phase shifted to higher temperatures and the dielectric constant of the core phase increased by re-oxidation treatment. It is considered that the  $T_c$  shift to higher temperatures of the shell phase is due to the increase of Ho acceptor and the oxidation of V<sup>3+</sup> to V<sup>4+</sup> or V<sup>5+</sup>. It is also expected that the increase of dielectric constant of the core phase is due to the decrease of oxygen vacancy concentration. Therefore, further investigation of the physical and chemical properties such as the compositional distribution, the concentration of the additives, and the occupational sites of the rare-earth ions in the shell phase is still necessary to understand the re-oxidation effect on the electrical properties of Ni-MLCCs.

#### 4 Conclusion

The effect of re-oxidation treatment on the solubility in dopants and the dielectric properties in La-V- and Ho-V-substituted BaTiO<sub>3</sub> solid solutions was investigated. By re-oxidation

treatment, Ho-V-substituted samples showed an increase of the lattice parameter in the range above  $x=0.015$ . The ESR spectra of V<sup>4+</sup> in Ho-V-substituted samples appeared in the range above  $x=0.015$  by re-oxidation treatment. It is considered that the increase of the lattice parameter by re-oxidation is due to the change of preferential occupational site of Ho ion from *A*-site to *B*-site along with precipitation of BaVO<sub>3</sub> or Ba<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> phase, so that oxidation of V<sup>3+</sup> to V<sup>4+</sup> or V<sup>5+</sup> increases with increasing Ho-acceptors. The  $T_c$  of Ho-V-substituted samples shifted to higher temperatures by increasing the doped content above  $x=0.015$  by re-oxidation treatment, while La-V-substituted samples showed a little change. It is considered that the decrease of  $T_c$  is attributed to *A*-site occupation of rare-earth ion, and the increase of  $T_c$  is due to the change of preferential occupational site of Ho ion from *A*-site to *B*-site and oxidation of V<sup>3+</sup>.

The effect of re-oxidation treatment on the electrical properties and microstructure in Ni-MLCC samples was also examined. MLCC samples containing V showed larger difference in the dielectric characteristics by re-oxidation compared with Mn-doped samples. Furthermore, Ho-V- and Yb-V-doped MLCC samples with 0.25 atomic% V showed larger increase of the dielectric constant at around 120 °C compared with La-V-doped samples. In the case of Ho-V-doped BT based MLCC samples, the impedance analysis at elevated temperature revealed that the  $T_c$  of the shell phase shifted to higher temperatures and the dielectric constant of the core phase increased by re-oxidation treatment. As a result, it was confirmed that the change of the occupational sites of rare-earth ions in BT lattice strongly affected the valency of acceptors and resultant dielectric properties of X7R Ni-MLCCs by re-oxidation treatment.

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