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Occupational sites and dielectric properties of rare-earth and Mn substituted $BaTiO_3$

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Abstract

The effect of re-oxidation treatment on the solubility in dopants and the dielectric properties of La–Mn- and Ho–Mn-substituted $BaTiO_3$ (ABO_3) was investigated. The lattice parameter and electrical resistivity results indicated that La ions occupied *A*-sites and Ho ions occupied both *A*- and *B*-sites. In the case of Ho–Mn-substituted samples, the decrease in lattice parameter and a shift of the Curie point (T_c) to higher temperatures by re-oxidation treatment were observed in the range in which Ho ions predominantly occupy *B*-sites (act as acceptors). On the other hand, La–Mn-substituted samples showed little change. Electron spin resonance measurements revealed that these changes due to re-oxidation were based on the decrease of the ionic size of Mn due to the oxidation of Mn^{2+} to Mn^{3+} or Mn^{4+}. The occupational sites of Ho ions strongly affected the valence state of Mn and the dielectric properties of $BaTiO_3$. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, multilayer ceramic capacitors (MLCs) with Ni internal electrodes composed of about 400 dielectric layers of below 2 μm thickness have been developed. To produce such thin-dielectric-layer MLCs with highly reliable electrical characteristics, many studies have been done on the dielectric materials focussing on the degradation mechanism. In nonreducible $BaTiO_3$ (ABO_3) based dielectric materials, 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.[1,2] Saito et al. reported that highly reliable Ni-MLCs conforming to X7R specification were obtained, using $BaTiO_3$–MgO–Ho_2O_3 based dielectrics, in combination with a re-oxidation treatment at the cooling stage below 1000°C during the firing process.[3] Resistivities of the dielectrics were increased by the addition of Ho_2O_3 when they were treated in an oxidizing atmosphere in the cooling stage. Kishi et al. reported the solubility of Mg and the rare-earth element into $BaTiO_3$ lattice.[4] It was confirmed that the larger ionic size rare-earth ions (La, Sm) predominantly dissolved in *A*-sites, and acted as donors, and the intermediate ionic size rare-earth ions (Dy, Ho, Er) dissolved in both the *A*-sites and *B*-sites, and acted as both donors and acceptors.

Albertsen et al. reported the changes in the Curie point (T_c) and the sample length under reduction and re-oxidation of $BaTiO_3$ ceramics containing Mn acceptors and various donor dopants on *B*-sites.[5] 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+}. These results indicate that the change of dielectric properties between the reduced and the re-oxidized state is strongly affected by the valence change of acceptor dopant and the ratio of donor/acceptor dopant. Thus, in the case of rare-earth and acceptor co-doped $BaTiO_3$ based systems, understanding the effect of both the valence of acceptor dopant and the ratio of occupational sites of rare-earth elements on the dielectric properties is important to control the electrical properties of Ni-MLCs.

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It is well known that Mn ions in $BaTiO_3$ lattice act as divalent acceptors like Mg ions on *B*-sites under the reducing condition, and Mn^{2+} is easily oxidized to Mn^{3+} or Mn^{4+} by re-oxidation treatment, while Mg maintains a constant valency of 2+. Therefore, in the present study, using two kinds of rare-earth element (La and Ho) and valence-unstable Mn acceptor, we investigated the effect of re-oxidation treatment on the solubility of dopants and the dielectric properties of La–Mn- and Ho–Mn-substituted $BaTiO_3$ solid solutions, assuming the shell phase of $BaTiO_3$–MnO-rare-earth based X7R dielectrics.

2. Experimental

Samples were prepared according to the formula $(Ba_{1-2x}R_{2x})(Ti_{1-x}Mn_x)O_3$; where R = La or Ho, x = 0~0.10. This formula is based on a model substituting rare-earth and Mn ions for Ba and Ti, respectively. The raw materials, $BaCO_3$, MnO, TiO_2, La_2O_3 and Ho_2O_3 were mixed and then calcined at 1250°C. The calcined powder containing an organic binder was pressed into disks, and then the disks were fired at 1380°C in a low oxygen atmosphere controlled by H_2, N_2, O_2 and H_2O (Po_2 of approximately 10^{-11} Pa) after the binder was burned out. Re-oxidation of the disks was carried out at 1250°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 dielectric properties of the samples were measured using a LCR meter. The electrical resistivity of the samples was measured by the two-probe dc technique. The ceramics were crushed and ground into a powder, and the identification of crystalline phases and the phase transition of the samples were characterized by powder X-ray diffraction (XRD) analysis and differential scanning calorimetry (DSC), respectively. The solubility of La, Ho and Mn into $BaTiO_3$ was determined by the behavior of the lattice parameters as a function of the doped amount x. In order to avoid the influence on the lattice parameters due to phase transition, high-temperature powder XRD analysis was carried out at 300°C which was much higher than the Curie point. The lattice parameters were determined precisely using the whole-powder-pattern decomposition method (WPPD[6]) program as described in a previous paper.[7] The valence state of Mn ions of the samples was confirmed by X band electron spin resonance (ESR) measurement.

3. Results and discussion

Changes of the microstructure and crystalline phases of the samples were not observed by re-oxidation treatment. The grain size of La–Mn-substituted samples increased a little with increasing doped content (about 2–5 μm), whereas that of Ho–Mn-substituted samples decreased with increasing doped content (about 20–2 μm). No secondary phase appeared in the range up to $x = 0.100$ for the La–Mn-substituted samples. On the other hand, in the case of Ho–Mn-substituted samples, a single phase of $BaTiO_3$ solid solution was obtained only up to $x = 0.010$, and the pyrochlore ($Ho_2Ti_2O_7$) phase appeared as a secondary phase from $x = 0.015$.

The effect of re-oxidation treatment on the solubility of dopants in La–Mn- and Ho–Mn-substituted $BaTiO_3$ solid solutions was investigated. The ionic radii of Ba, Ti, La, Ho and Mn are summarized as follows: *A*-site (12 coordinate): $Ba^{2+} = 1.610$ Å, $La^{3+} = 1.360$ Å, $Ho^{3+} = 1.234$ Å; and *B*-site (6 coordinate): $Ti^{4+} = 0.605$ Å, $La^{3+} = 1.032$ Å, $Ho^{3+} = 0.901$ Å, $Mn^{2+} = 0.670$ Å, $Mn^{3+} = 0.580$ Å, $Mn^{4+} = 0.530$ Å. 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.[8] The substitution sites were determined based on the change of the lattice parameter. Fig. 1 shows the lattice parameters of the samples measured at 300°C, as determined by WPPD. La–Mn-substituted samples showed little change in the lattice parameter by re-oxidation treatment, while Ho–Mn-substituted samples showed a large difference. In the case of La–Mn-substituted samples, the lattice parameter decreased monotonously as a function x. This indicated that La ions mainly occupied the *A*-site accompanied by B-site occupation of Mn^{2+} ions. In the case of the reduced state Ho–Mn-substituted samples, the change in lattice parameter behavior is divided into three stages. Initially, the lattice parameter decreased gradually up to $x = 0.010$, and then showed little change up to $x = 0.020$. In the third stage, the increase in the

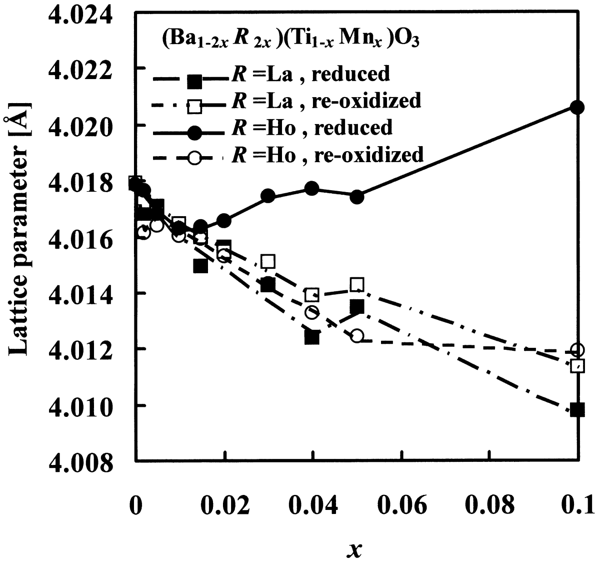
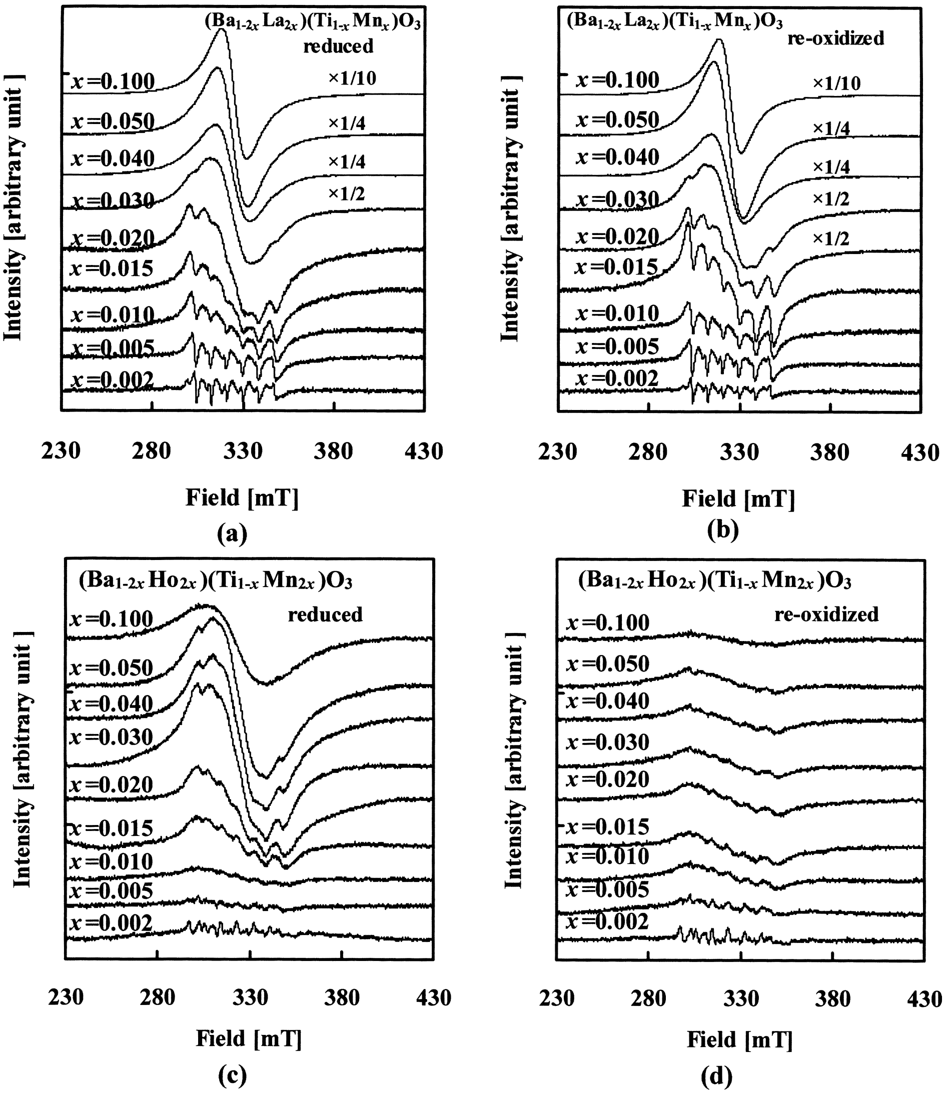


Fig. 1. Lattice parameter of $(Ba_{1-2x}R_{2x})(Ti_{1-x}Mn_x)O_3$ solid solutions measured at 300°C (R = La, Ho).

lattice parameter was observed up to $x=0.100$. Thus, the change of the lattice parameter for the reduced state Ho–Mn-substituted samples is considered as follows. In the first stage, Ho mainly occupied the *A*-site accompanied by *B*-site occupation of Mn^{2+} ions. The occupation ratio of Ho in the *A*-site decreased during the second stage and then Ho ions mainly occupied the *B*-site along with Mn^{2+} ions in the third stage. The difference of lattice parameter between the reduced state and the re-oxidized state Ho–Mn-substituted samples was observed above $x=0.020$. The decrease of the lattice parameter by re-oxidation treatment increased with increasing doped content.

To clarify the effect of Mn on the change of the lattice parameter by re-oxidation treatment, the valency of Mn was examined. Fig. 2 shows ESR spectra of the reduced state and the re-oxidized state samples. In the case of the reduced state samples, the intensity of ESR spectra of Mn^{2+} increased by increasing the amount doped. By re-oxidation treatment, La–Mn-substituted samples showed little change in the ESR spectra, while Ho–Mn-substituted samples showed a large difference. In the case of Ho–Mn-substituted samples, the intensity of ESR spectra of Mn^{2+} was strongly depressed in the range above $x=0.015$ by re-oxidation treatment. This indicated that a portion of doped Mn^{2+} ions were oxidized to Mn^{3+} or Mn^{4+}. Thus, it is considered that the decrease of the lattice parameter of Ho–Mn-substituted samples by re-oxidation treatment is based upon the decrease of the ionic size of Mn ions due to the valence change of Mn^{2+} to Mn^{3+} or Mn^{4+}.

The electrical resistivity of the reduced state samples measured at room temperature is shown in Fig. 3. The change in resistivity almost correspond to the change



(a) (b) (c) (d)

Fig. 2. ESR spectra of $(Ba_{1-2x}R_{2x})(Ti_{1-x}Mn_x)O_3$ solid solutions as a function of x. (a) R = La, reduced state; (b) R = La, re-oxidized state, (c) R = Ho, reduced state; (d) R = Ho, re-oxidized state.

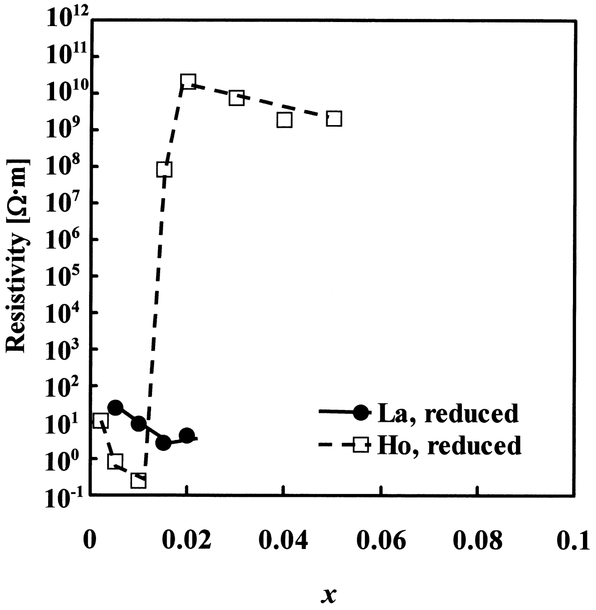


Fig. 3. Resistivity of $(Ba_{1-2x}R_{2x})(Ti_{1-x}Mn_x)O_3$ solid solutions sintered at 1380°C in reducing atmosphere as a function of x (R = La, Ho).

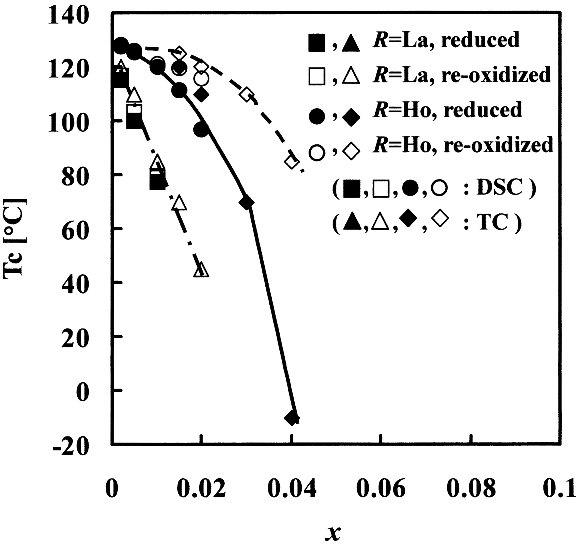


Fig. 4. Change in the T_c of the reduced and the re-oxidized state $(Ba_{1-2x}R_{2x})(Ti_{1-x}Mn_x)O_3$ solid solutions as a function of x (R = La, Ho).

of the lattice parameter for each sample. All La–Mn-substituted samples were semiconductive because the color of the sintered body was dark, though the resistivity was not obtained because of deformation of the ceramics for samples above $x = 0.020$. This indicated that La ions predominantly acted as donor dopants. On the other hand, in the case of Ho–Mn-substituted samples, the resistivity jump was observed at $x = 0.015$. This resistvity jump was attributed to the change of the predominant occupational sites of Ho ions, from the A-site (act as a donor) to the B-site (act as an acceptor).

The T_c of the reduced state and the re-oxidized state samples was determined by DSC and dielectric measurement. DSC was carried out for samples with lower electrical resistivites, for which it is impossible to measure dielectric properties. Fig. 4 shows the T_c shift of the reduced state and the re-oxidized state of the samples. In the case of La–Mn-substituted samples, T_c decreased almost linearly with increasing doped content. On the other hand, the slope of the T_c shift of Ho–Mn-substituted samples became steeper with increasing doped content. By re-oxidation treatment, the T_c of the Ho–Mn-substituted samples shifted to higher temperatures with increasing doped content above $x = 0.015$, while the change in T_c of the La–Mn-substituted samples was not observed. These results correspond well with the results of the lattice parameters. Thus, it is considered that the smaller ionic size Mn^{3+} and Mn^{4+} ions induce the shift of T_c by re-oxidation treatment.

The lattice parameter as well as the T_c measurements indicated the effect of valence change of Mn ions by re-oxidation treatment. In the case of La–Mn-substituted samples, the changes in the lattice parameters and T_c were not observed. It is expected that La-donors compensate Mn-acceptors. On the other hand, in the case of the Ho–Mn-substituted samples with smaller doped content below $x = 0.010$, the changes in the lattice parameters and T_c were not observed. As mentioned above, Ho ions mainly act as donor dopants up to $x = 0.010$ and as acceptor dopants above $x = 0.020$. Thus, in the Ho–Mn-substituted $BaTiO_3$ system, it is expected that Ho-donors compensate Mn-acceptors in the range up to $x = 0.010$ and excess Mn-acceptors increase with increasing Ho-acceptors in the range above $x = 0.020$. Albertsen et al. reported that Mn^{2+} could not be oxidized in donor-acceptor charge complexes, and the T_c of reduced and re-oxidized material coincided for equivalent concentrations of Mn-acceptor and donor.[5] The present results showed good agreement with the result of Albertsen et al., and can be explained as follows. In the case of La–Mn-substituted samples, donor-acceptor complexes $[2La_{Ba}^{\cdot}\text{-}Mn_{Ti}'']$ prevent valence change of Mn^{2+}, so that the differences of both the lattice parameters and the T_c between the reduced state and the re-oxidized state are negligible. On the other hand, in the case of Ho–Mn-substituted samples, for equal concentrations of Ho-donors and Mn^{2+}-acceptors, donor-acceptor complexes $[2Ho_{Ba}^{\cdot}\text{-}Mn_{Ti}'']$ are formed in the range up to $x = 0.010$, so that oxidation of Mn^{2+} is prevented. In the range above $x = 0.020$, as Ho-acceptors increase, the differences of both the lattice parameters and the T_c between the reduced state and the re-oxidized state increase with increasing free Mn^{2+} which can be oxidized to Mn^{3+} or Mn^{4+}. Consequently, it was confirmed that the change of the occupational sites of Ho ions in $BaTiO_3$ lattice strongly affected the valence state of acceptor ions and resultant dielectric properties.

4. Conclusion

The effect of re-oxidation treatment on the solubility in dopants and the dielectric properties in La–Mn- and Ho–Mn-substituted $BaTiO_3$ solid solutions was investigated. High-temperature powder XRD analysis revealed that La ions occupy *A*-sites and Ho ions occupy both *A*- and *B*-sites. The resistivity results also indicated that Ho ions mainly act as donor dopants up to $x=0.010$ and as acceptor dopants above $x=0.020$. By re-oxidation treatment, Ho–Mn-substituted samples showed a decrease of the lattice parameter in the range above $x=0.020$, while La–Mn-substituted samples showed no change. The intensity of ESR spectra of Mn^{2+} in Ho–Mn substituted samples was strongly depressed in the range above $x=0.015$ by re-oxidation treatment. The T_c of Ho–Mn-substituted samples shifted to higher temperatures by increasing the amount doped above $x=0.015$ by re-oxidation treatment, while La–Mn-substituted samples showed no change. It is considered that the changes in the lattice parameter and the T_c of Ho–Mn substituted samples by re-oxidation is based upon the decrease of the ionic size of Mn due to the valence change of Mn^{2+} to Mn^{3+} or Mn^{4+}. Moreover, these results suggested that the formation of the donor-acceptor complexes prevent the valence change of Mn^{2+} in rare-earth and acceptor co-doped $BaTiO_3$ based systems. It was determined that the occupational sites of Ho in $BaTiO_3$ lattice strongly affected the valence state of acceptors and the dielectric properties. 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 necessary to understand the re-oxidation effect on the electrical properties of Ni-MLCs.

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