Control of the doping sites of Ho$^{3+}$ in BaTiO$_3$ by a water-soluble precursor method

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1. Introduction

Barium titanate (BaTiO$_3$) is a representative electroceramic as it has been used for the major component of multi-layer ceramic capacitors (MLCCs). BaTiO$_3$ is an excellent insulator with the stoichiometric composition, whereas it becomes an n-type semiconductor when some types of defects are introduced such as oxygen vacancies and heterovalent substituents of trivalent rare-earth (RE) ions for Ba$^{2+}$ or pentavalent cations for Ti$^{4+}$.[1-3] Such a semiconductor nature is used in, for example, the positive temperature coefficient resistor (PTCR) application.

In practical use, various types of dopants are added in BaTiO$_3$-based ceramics to control the electric properties. For example, Mn is a dopant which enhances the tolerance against the reducing treatment by replacing Ti$^{4+}$ as acceptors.[4] REs typically have the oxidation state of $+3$ with some exceptions such as Eu$^{3+}$ and Ce$^{4+}$. Both the valence of $+3$ and the ionic radii are intermediate between those of Ba$^{2+}$ and Ti$^{4+}$ and, therefore, RE$^{3+}$ can occupy either of the A or B site in the ABO$_3$-type BaTiO$_3$ lattice. The doping behavior of RE$^{3+}$ is somewhat complicated and it is affected by a Ba/Ti ratio, the ionic size of RE$^{3+}$ and the atmosphere.[12,13][5-11] The several thorough investigations have led to well-accepted conclusions about the doping-related phenomena of REs as follows. The larger RE$^{3+}$ such as La$^{3+}$ and Sm$^{3+}$ prefers the 12-coordinated Ba site to occupy, while the smaller Yb$^{3+}$ and Lu$^{3+}$ preferentially replace the 6-coordinated Ti site. The lanthanides between Gd$^{3+}$ and Tb$^{3+}$ exhibit an amphoteric nature which is a nature that they could enter in either/both the Ba or/and Ti site(s) depending on the Ba/Ti ratio. The Ba-rich or Ti-rich condition brings a tendency of entering in the Ti site or Ba site, respectively. Makovec et al.[12,13][14-15] investigated the solid solubility of La, Ho, Y and Dy in BaTiO$_3$ by compositional analysis with quantitative electron-probe microanalysis (EPMA). They verified rather high acceptability to rare-earth dopants of the BaTiO$_3$ lattice. According to them, the solubility limits were dependent on the Ba/Ti ratio and the composition at the maximum concentration of La-doped BaTiO$_3$ was determined as Ba$_{0.70}$La$_{0.30}$Ti$_{0.925}$(V$_{Ti}^{+}$)$_{0.075}$O$_3$ (at 1400°C).[12] They referred to the site preference of several lanthanides. For Ho$^{3+}$ in BaTiO$_3$, the composition at the maximum concentrations were to be Ba$_{0.10}$Ho$_{0.90}$Ti$_{0.995}$(V$_{Ti}^{+}$)$_{0.001}$O$_3$ (at 1400°C) for the Ba site substitution, Ba$_{0.92}$Ho$_{0.08}$(V$_{Ti}^{+}$)$_{0.02}$O$_3$ (at 1500°C) for the Ti site substitution and Ba$_{0.958}$Ho$_{0.04}$(C$_{15}$/C$_{15}$)$_{0.08}$O$_{3}$ for the Ba and Ti sites substitution.[12,13][14]

An important point is that the expected electric properties are completely different depending on the substitution site of RE$^{3+}$. The conventional Kröger-Vink notation explains the n-type semiconductivity by replacing Ba$^{2+}$ with RE$^{3+}$ with the extra charge being electronically compensated as mentioned later. On the other hand, RE$^{3+}$ behaves as acceptors trapping the carrier electrons to passivate the donors when they replace Ti$^{4+}$. The case of equally replacing both Ba$^{2+}$ and Ti$^{4+}$ does not require further charge compensation and, then, the doped BaTiO$_3$ should remain an insulator. These mean that the electric properties of BaTiO$_3$-based ceramics can be controlled with a single type of an amphoteric RE dopant from semiconducting to insulating with the substitution sites.

BaTiO$_3$-based ceramics in industry are mainly fabricated by a solid state reaction method because of the suitability for mass-production. A general disadvantage of this process is the compositional inhomogeneity in the starting raw powders. The size dimensions of the compositional homogeneity cannot be smaller than the particle sizes of the raw powder particles. The reaction between the constituents in the starting powder mixture starts at the contacts between the powder particles. It usually requires heat treatment at high temperatures for a long period of time to obtain a compositionally equilibrated body to allow the reaction and migration of the constituent atoms. For example, Liu et al. obtained Ho$-$BaTiO$_3$ at the highest concentration of 15 at.% at a temperature as high as 1550°C with the duration for a few days.[14] On the other hand, such high temperature treatment
might lead to compositional deviation from the starting mixture during the treatment because of the moderate vapor pressure of the constituents such as BaO (ca. 3 Pa at 1500°C).\textsuperscript{19} Formation of eutectic compounds in the BaO–TiO\textsubscript{2} system (Fig. 213 in Ref. 17) and H\textsubscript{2}O\textsubscript{2}–TiO\textsubscript{2} system (Fig. 6478 in Ref. 18) would complicate the situations if they form during high temperature treatment before reaching the compositional equilibrium. Therefore, a precursor is quite advantageous, which offers better control on the doping phenomena without elaboration as very high temperature and careful heat-treatment sequence to avoid forming secondary phases.

We have recently developed a new water-soluble precursor for BaTiO\textsubscript{3}.\textsuperscript{19} That is based on citratoperoxotitanium ammonium\textsuperscript{20,21} for a Ti source and a barium salt (nitrate or citrate) for a Ba source. It is somewhat similar to Pechini route in terms of using citric acid to stabilize a Ti source\textsuperscript{22,23} but to use metal Ti power is characteristic instead of using titanium tetraisopropoxide, a popular Ti source in sol–gel processes. The process is completely based on aqueous solution and chemically unstable species such as metal alkoxides are not involved. In our previous report revealed that the aqueous solution of the precursor is stable over years without forming any precipitate, which assures the compositional consistency during preparation and preservation.

In this work, we focus on the compositional homogeneity of the solution for the precursor of doped BaTiO\textsubscript{3}. The constituent cations are expected to be uniformly dispersed in the aqueous solution in the size dimension of molecules and ions. It leads to shorter time and lower temperature for reaching the compositional equilibrium for the RE-doped BaTiO\textsubscript{3}. We demonstrate that the substitution site control simply with the starting compositions of the solution and, here, Ho is chosen for an amphoteric dopant. The knowledge obtained with Ho will be applicable for other REs with similar ion radii and substitution sites.

2. Experimental

The water-soluble precursor was prepared by the method previously reported in Ref. 19. A typical synthetic procedure is as follows. 10 mmol of Ti powder (99%, Wako Chemical, Japan) was solved as peroxotitanium complex ions in a mixed solution of 50 mL H\textsubscript{2}O\textsubscript{2} aq. (38%, Kanto Chemical, Japan) and 10 mL ammonia solution (18%, Kanto Chemical, Japan). The peroxotitanium complex was stabilized by citric acid at a ratio of Ti: citric acid = 1:5. Ho\textsubscript{2}O\textsubscript{3} (99.9%, Kanto Chemical, Japan) was used for a Ho source. It was solved in nitric acid (38%, Kanto Chemical, Japan) at 80°C. The excess nitric acid was removed by evaporating the solvent to dryness on a hot plate. The obtained holmium nitrate was solved in water. BaCO\textsubscript{3} was solved in an aqueous solution of citric acid at a ratio of Ba: citric acid = 1:5. Then, the three solutions were mixed together. The mixed solution was condensed to glue-like sticky-gel by evaporating the solvent. The sticky gel was carefully heated on an evaporating dish to char the organic component and, then, treated in air at 800°C for 1 h to burn out the organic component. The obtained white powder after the treatment at 800°C was pressed into a 10 mm\textsuperscript{3} compact under 15 MPa with adding a small amount of polyvinyl alcohol (Kuraray PVA-217, Japan) solution as a binder. The compact was calcined at 500°C in air for 1 h to remove the binder and sintered at 1375°C for 6 h in air.

In order to control the substitution sites, precursor solutions were prepared in three different compositions. They were (A) Ba\textsubscript{1-x}Ho\textsubscript{x}TiO\textsubscript{3} (A-site substitution), (B) BaTi\textsubscript{1-x}Ho\textsubscript{x}O\textsubscript{2} (B-site substitution) and (C) Ba\textsubscript{1-2x}Ti\textsubscript{1+x/2}O\textsubscript{2} (A/B both sites substitution). Hereafter, they are referred to as (A) A-site, (B) B-site and (C) A/B-sites substitution.

The prepared samples were characterized by XRD (Rigaku Ultima IV, Japan) with CuK\textsubscript{α} radiation. KCl was used for an internal standard to calibrate the peak position of 2θ. The microstructures were observed with SEM (JEOL JSM-T330, Japan). The elemental mapping was examined with EDS (Oxford Link ISIS 300, UK) equipped to SEM. The XAFS experiments were performed at Beam Line–7C, 9A and 9C in KEK PF, Japan. For the XAFS experiments, Sm\textsuperscript{3+}-doped and Yb\textsuperscript{3+}-doped BaTiO\textsubscript{3} were measured for comparison to confirm the substitution sites as discussed later. The X-ray absorption spectra were measured at the Ln L\textsubscript{III} edges (Ln = Ho, Sm and Yb) in the fluorescent mode with a Lytle detector or a multichannel solid-state detector (SSD). Processing the collected data and the refinement were carried out with FEFF6.\textsuperscript{24}

The electric properties were characterized with an LCR meter (NF ZM-2371, Japan) on the sintered disks with forming the Au electrodes on the pellet surfaces by an ion coater (Eiko Engineering IB-3, Japan). To investigate the charge compensation mechanisms, the electric properties were measured in the as-prepared state and after annealing in Ar at 500°C for 15 min.

3. Results and discussion

3.1 XRD and SEM-EDS studies

Figure 1 compares the XRD patterns of Ho-BaTiO\textsubscript{3} (doping amount = 5 at%) prepared by the solid state reaction [Fig. 1(a)] and water-soluble precursor method with the three different doping manners.
and by the water-soluble precursor method [Fig. 1(b)] with
different doping manners of (A) A-site, (B) B-site and (C) A/B-
sites substitution. The samples by solid state reaction were pre-
pared through basically the same procedure as that described in
Experimental section except for using BaCO₃, TiO₂ and Ho₂O₃
for the starting materials. Small peaks of unidentified secondary
phases are recognized for each doping manner in the solid state
reaction [Fig. 1(a)]. It indicates that incorporating the foreign
cation of Ho³⁺ into the BaTiO₃ lattice is dif-

ferent in the solid state
reaction method regardless of the doping manner without elabo-
ration such as thorough mixing of ultra-
fine powders and long-
period of time sintering at high temperatures. On the other hand,
no distinct secondary phases are recognized in the samples
prepared from the water-soluble precursor for each of (A) A-site,
(B) B-site and (C) A/B-sites substitution. Although they seemed
to be composed of a single phase of the perovskite type structure,
small extra peaks were actually observed in the pattern for (A) A-
site substitution. Figure 2 shows the magnified patterns between
29 and 32° of Fig. 1(b). There exists a small impurity peak at
30.6° in (A) A-site substitution as indicated with the symbol (▼).

Figure 3 compares the results of elemental mapping for Ho in
the Ho–BaTiO₃ disks prepared from the water-soluble precursor
for (A) A-site [Figs. 3(a) and 3(b)], (B) B-site [Figs. 3(c) and
3(d)] and (C) A/B-sites [Figs. 3(e) and 3(f)] by SEM-EDS. The Ho concentration was 5 at%. Ho uniformly distributes in
Figs. 3(d) and 3(f), whereas agglomerations of Ho were recog-
nized for (A) A-site substitution [Fig. 3(b)]. Here, note that the
observed surfaces were chemically etched by a solution of HF
aq.:HNO₃ aq.:H₂O = 1:3:6 mL for a several seconds after wrap-
ing to emphasize the grain edges. The surface roughness and
agglomeration of the Ho compounds were emphasized by
chemically removing the BaTiO₃ matrix with the embedded Ho
compounds emerging to the surface in Fig. 3(b).

The results of this observation are consistent with XRD (Fig. 2).
It suggested the existence of the secondary phase only in the (A)
A-site substituted sample. These indicate that Ho³⁺ was success-
fully incorporated in the BaTiO₃ lattice for (B) B-site and (C) A/
B-sites substitution at least up to 5 at%, and the solubility limit of
Ho in the A site was less than 5 at%.

Figure 4 shows the variation of the lattice constants with the
Ho doping, which were evaluated with the peak positions of the
200 and 002 reflections of BaTiO₃. The lengths of the a and c
axes of the unit cells are plotted in Fig. 4(a) and the change of the
unit cell volumes is shown in Fig. 4(b). The ionic size of Ho³⁺ is
smaller and larger than Ba²⁺ and Ti⁴⁺, respectively, and, then,
The lattice is expected to shrink and expand, depending on which
of Ba²⁺ and Ti⁴⁺ it replaces. From this point, the result of (B) B-
site substitution was easily explainable. The length of the a axis
expanded as Ho doping with the c axis approaching to the a axis
by reducing its length gradually. The unit cell volumes expanded

![Fig. 3. Microscopic elemental mapping of Ho by SEM-EDS.](image)

![Fig. 2. Magnified patterns of Fig. 1(b) in the 2θ range between 29 and 32°.](image)
nearly monotonically reflecting successful substitution for Ti$^{4+}$ by larger Ho$^{3+}$. The tendency was consistent with the report on BaTi$_{1-x}$Ho$_x$O$_3$ by Liu et al.\textsuperscript{15)}

The small change in the unit cell dimensions for (A) A-site substitution was interpreted to be due to the limitation of solubility of Ho$^{3+}$ in the Ba site. The tendency of (C) A/B-sites substitution looks similar to (A) A-site substitution but the electric properties discussed later revealed that the effects of the substitution was completely different. The nearly unchanged cell dimensions was interpreted as a consequence of balanced effects of shrinkage and expansion with the Ba$^{2+}$ and Ti$^{4+}$ substitution.

Further addition of Ho$^{3+}$ made difference of the effects of the doping manner clear. Figure 5 shows the XRD patterns of 10 at% doped BaTiO$_3$. (C) A/B-sites substitution does not exhibit any secondary phases even at 10 at%. (B) B-site substitution brought the coexistence of the hexagonal BaTiO$_3$ phase. For (A) A-site substitution, the further addition resulted in the evolution of the impurity peak around 30.6° already recognized in Fig. 2. Makovec et al.\textsuperscript{14)} investigated the solubility limits of several lanthanides in BaTiO$_3$ by microscopic compositional analysis and concluded that the solubility of the amphoteric REs such as Ho$^{3+}$ in the A-site was below ~1.5 at% as Ba$_0.985$RE$_{0.015}$Ti$_{0.996}$(V$_{Ti}^{0.004}$)$_{0.004}$O$_3$ with the charge compensated by V$_{Ti}^{0.004}$. Ho$^{3+}$ could enter in the B-site as much as ~15 at% with involving oxygen vacancies as Ba$_{0.85}$RE$_{0.15}$O$_{2.925}$(V$_{O}^{0.07}$). The highest solubility of Ho$^{3+}$ was ~24 at% which was attained with Ho$^{3+}$ distributing at the A-site as high as ~9 at% and the B-site as high as ~15 at% as the composition of Ba$_{0.91}$Ho$_{0.09}$Ti$_{0.85}$O$_{2.97}$(V$_{O}^{0.03}$). The estimated solubility in this work is consistent with the report by Makovec et al. It is in the order of (C) A/B-sites, (B) B-site and (A) A-site substitution. The solubility limit of (C) A/B-sites substitution is more than 10 at% and this is understood by the fact that no extra charge compensation is necessary for this type of substitution [see Eq. (4) in 3.3]. The solubility limits for (A) A-site was roughly less than 3 at%. High concentration doping for (B) B-site substitution brought the formation of the hexagonal polymorph which, on the other hand, was proposed to be a metastable phase gradually changing to the perovskite-type structure with the heat-treatment.\textsuperscript{15)}

### 3.2 XAFS study

In order to confirm the substitution sites, the XAFS analysis was carried out. The Ba atoms are placed at the 12 coordinated sites in the perovskite type BaTiO$_3$, constructing a nearly cubic-close-packing arrangement with the O atoms. The interatomic distance between Ba$^{2+}$ and O$^{2-}$ is approximated to 2.83\AA. On the other hand, the Ti atoms are coordinated by six O$^{2-}$ ions with the interatomic distance of ca. 2.01\AA.\textsuperscript{25)} The local structure analysis by XAFS could offer a rather direct information about the substituting sites of the doped RE$^{3+}$.

As discussed in 3.1, the solubility limit of Ho$^{3+}$ in (A) A-site substitution was estimated to be just above 1 at%. We have encountered difficulty in detecting the EXAFS (extended X-ray absorption fine structure) signals from Ho$^{3+}$ in the A site because

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**Fig. 4.** Variation of the lattice dimensions against the Ho concentration. (a) lattice constants $a$ and $c$ and (b) unit cell volume. Triangles (▲ and △): undoped BaTiO$_3$, circles (● and ○): (A) A-site substitution, diamonds (◆ and ◇): (B) B-site substitution and squares (■ and □): (C) A/B-sites substitution. Solid and open symbols in (a) indicate the $a$ and $c$ axes, respectively.

**Fig. 5.** XRD patterns of 10 at% added Ho-doped BaTiO$_3$ for (A) A-site, (B) B-site and (C) A/B-sites substitution.
Radial distribution functions of the for (A) A-site substitution. The doping concentration was 5 at.

The incorporation of these lanthanides in the BaTiO$_3$ Ho and Yb L$_{III}$ edges for (B) B-site substitution and at the Sm L$_{III}$ edge EXAFS against the ionic radii in the literature. The Roman numerals in (c) Ba$_2$TiO$_3$ for (A) A-site substituted sample at the concentration of 5a.

The ionic radius of Sm$^{3+}$ was determined by the EXAFS refinement against the ionic radii after the Fourier transformation on the $k^2$-EXAFS oscillations. The distinct contributions due to the neighboring O atoms are around 1.8 Å for (B) B-site substituting Yb$^{3+}$ and Ho$^{3+}$, whereas a rather broad contribution of the O shell is recognized between 1.1 and 3.0 Å for (A) A-site substituting Sm$^{3+}$. The phase shift was not corrected in Fig. 6(b) and the contributions of the surrounding shells appear on the shorter side of the interatomic distance than the true values. The scattering power of lighter atoms for X-ray weakens as the interatomic separation and it is attributed to the broadness and the weakness of the contribution of the O shell in Fig. 6(b) for the A-site substituting Sm$^{3+}$.

Figure 6(c) is a plot of the Ln$^{3+}$-O$^{2-}$ interatomic distances determined by the EXAFS refinement against the ionic radii after Shannon. A linear relationship can be seen in the ionic radii from Ti$^{4+}$ to Ba$^{2+}$ through Yb$^{3+}$, Ho$^{3+}$ and Sm$^{3+}$. The boundary of the site preference between the 12-coordinated Ba site and the 6-coordinated Ti site is estimated to exist around 1.1 Å of the ionic radius.

### 3.3 Electric properties and charge compensation mechanism

The capacitance measurements were carried out to characterize the electric properties, which could provide information about the defects relating to the charge compensation. Figures 7(a) and 7(b) show the temperature dependence of the relative dielectric constant, $\varepsilon_\infty$, and the dielectric loss, tan $\delta$, at 1 kHz for undoped BaTiO$_3$ and 1 at.

The boundary of the site preference between the 12-coordinated Ba site and the 6-coordinated Ti site is estimated to exist around 1.1 Å of the ionic radius.

It was found that (A) A-site substitution changed its electric properties after annealing in Ar at a modest temperature of 500°C. Figure 7(c) shows $\varepsilon_r$ and tan $\delta$ of the A-site substituted sample (A) after the anneal. Comparison between Figs. 7(a) and 7(c) clearly shows that the insulating as-prepared sample became semiconductive after the anneal with showing apparently large $\varepsilon_r$ with large tan $\delta$ of, for example, 0.98 at room temperature [Fig. 7(c)]. Here, note that the anomalously large $\varepsilon_r$ is due to the semiconductive nature of the sample and the values themselves are not meaningful. The (B) B-site and (C) A/B-sites substitution did not show such semiconductivity even after the anneal of the same conditions.
Possible charge compensation mechanisms are discussed here for the doped BaTiO$_3$ to interpret the above results. For (A) A-site substitution, the excess positive charge with trivalent Ho$^{3+}$ replacing divalent Ba$^{2+}$ would be simply compensated by one Ti$^{4+}$ reducing its charge to Ti$^{3+}$ as Eq. (1). The formation of Ti$^{2+}$ results in releasing an electron from one Ti$^{3+}$ as expressed in Eq. (2) and, hence, brings n-type semiconductivity to the material.

\[ \text{Ho}_2\text{O}_3 + 2\text{Ti}^2\text{O}_2 \rightarrow 2\text{Ho}_2^*\text{O}_3 + 2\text{Ti}_\text{Ti}^* + 6\text{O}_\text{O}^* + 1/2\text{O}_2 \uparrow \]  
\[ \text{Ti}_\text{Ti}^* \rightarrow \text{Ti}_\text{Ti}^* + e^- \]  

However, as shown in Fig. 7, the as-prepared sample (A) was an insulator and it became semiconductive after annealing in Ar [Fig. 7(c)]. The insulating nature is due to the charge compensation by the cation vacancies [Eq. (3)] rather than Eq. (1), where the equal amount of Ba$^{2+}$ and Ti$^{4+}$ vacancies are formed in every 7 formula units of BaTiO$_3$. The change in the electric properties from insulating to semiconductive by annealing in Ar indicates that the charge compensation mechanism changed from Eqs. (3) to (1) (fully or partly) with releasing the oxygen atoms during the anneal.

\[ 3\text{Ho}_2\text{O}_3 + 6\text{Ti}^2\text{O}_2 \rightarrow 6(\text{Ho}_2^*\text{O}_3 + \text{Ti}_\text{Ti}^* + 3\text{O}_\text{O}^*) \]
\[ + (\text{V}_\text{Ba}^* + \text{V}_\text{Ti}^* + 3\text{O}_\text{O}^*) \]  

Mode switching from Eq. (1) (electronic) to Eq. (3) (ionic) in the charge compensation mechanism is recognized for A-site substituted La-doped BaTiO$_3$ depending on the La concentration. At the relatively lower concentrations, the electronic compensation [Eq. (1)] is considered to be dominant, bringing n-type semiconductivity even to the air-fired samples. Heavier doping leads to the ionic compensation [Eq. (3)] which does not involve carrier electrons and the boundary is considered as about 0.5 at%.

For the ionic compensation, Ti vacancies are proposed for the major charge compensator in the literature. The formation of Ti$^{3+}$ as Eq. (1) brings n-type semiconductivity to the material. More Ti$^{3+}$ is expected to occupy the sites 

\[ 2\text{BaO} + \text{Ho}_2\text{O}_3 \rightarrow 2\text{Ba}^*\text{O}_3 + 2\text{Ho}_2^* + 5\text{O}^* + \text{V}_\text{O}^* \]  

For (C) A/B-sites substitution, Ho$^{3+}$ is expected to occupy the both sites without extra charge compensation, assuming that it equally distributes at the Ba$^{2+}$ and Ti$^{4+}$ sites [Eq.(5)].

\[ \text{Ho}_2\text{O}_3 \rightarrow \text{Ho}_2^*\text{O}_3 + \text{Ho}_2^* + 3\text{O}^* \]  

Equations (4) and (5) indicate that electronic carriers are not involved in the charge compensation and the insulating nature of (B) B-site and (C) A/B-sites substitution is consistent with the defect equations. Although there is a possibility that the dopant enters in the other site with leaving vacancies on the targeting site, no distinct evidence was recognized relating to it in this work. Such a case was supposed to be minor even if it happened and the effects were considered negligibly small.

4. Conclusions

This work demonstrated the control of the doping sites of Ho$^{3+}$ in BaTiO$_3$ with the water-soluble precursor. The doping sites were carefully investigated with XRD, SEM-EDS, XAFS and the electric properties measurements.

XRD and SEM-EDS exhibited the difference in the solubility of Ho$^{3+}$ depending on the substitution site. The solubility was in descending order of the A/B-sites, B-site and A-site substitution and it agreed well with the previous findings in the literature. The
Yb precursor was advantageous to prepare RE-doped BaTiO3. XAFS analysis for the B-site substituted Ho–BaTiO3 as well as Yb–BaTiO3 (B-site substitution) and Sm–BaTiO3 (A-site substitution) revealed the different local environments around the lanthanides depending on the substitution site. The characterization on the electric properties presented possible charge compensation mechanisms associated with the substitution. As predicted from the charge compensation mechanisms, the sintered disks of the B-site and A/B-sites substituted samples showed an insulating nature. The A-site substitution brought n-type semiconductivity after annealing at 500°C in Ar.

These results revealed that the substitution sites were successfully controlled simply with the starting compositions of the solution and the compositional uniformity of the water soluble precursor was advantageous to prepare RE-doped BaTiO3.

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